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<b>(21) International Application Number:</b> PCT/US99/08320 <b>(22) International Filing Date:</b> 15 April 1999 (15.04.99) <b>(30) Priority Data:</b> 60/081,850      15 April 1998 (15.04.98)      US <b>(71) Applicant (for all designated States except US):</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> POPE, Timothy, J. [US/US]; 1308 Whitehall, Midland, MI 48642 (US). MERGENHAGEN, Laura, K. [US/US]; 324 Forest Drive, Lake Jackson, TX 77566 (US). <b>(74) Agent:</b> MCKINNEY, Osborne, K.; The Dow Chemical Company, Patent Dept., B-1211, 2301 Brazosport Boulevard, Freeport, TX 77541 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PEELABLE-SEAL POLYOLEFIN COMPOSITION AND SEALANT LAYER		
<b>(57) Abstract</b>  <p>The present invention relates to an olefin sealant composition and sealant layer having easy-open heat seal characteristics. The novel composition and sealant layer are made from at least one ethylene polymer, at least 25 weight percent (based on the total weight of the composition or layer) of at least one polybutylene polymer, a silica-containing or calcium-containing additive, a slip additive and optional quantities of an ethylene polymer as additive carrier resin. The preferred ethylene polymer is a homogeneously branched ethylene polymer and the preferred polybutylene polymer has a low crystallinity or high comonomer content. As a sealant layer, the composition has excellent hot tack properties, relative low coefficient of friction and especially exceptional sealing properties wherein its heat seal strength is in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at 100 °C and the statistical average deviation of its heat seal strength between 100 °C to 130 °C sealing temperatures is less than or equal to 16.5 percent. The composition is useful in applications that require consistent and stable peelable seal performance across broad sealing windows such as, for example, cereal box liners.</p>		

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PEELABLE-SEAL POLYOLEFIN COMPOSITION AND SEALANT LAYER

The present invention relates to an olefin sealant  
5 composition having easy-open heat seal characteristics and to  
a sealant layer comprising a plurality of olefin polymers.  
In particular, this invention pertains to a peelable seal  
composition and sealant layer comprised of at least one first  
ethylene polymer as a sealant base resin, at least 25 weight  
10 percent (based on the total weight of the composition or  
layer) of at least one polybutylene polymer, silica-  
containing or calcium-containing additive, a slip additive  
and optional quantities of a second ethylene polymer as an  
additive carrier resin and/or as an incompatibilizer for the  
15 first ethylene polymer.

Typically, peelable seals are functional heat seals  
designed to be opened with relative ease by the  
product/package consumer. The opening mechanism can be  
adhesive failure wherein the sealant layer delaminates from  
20 an adjacent substrate layer or, alternatively, cohesive  
failure wherein there is controlled failure within the  
sealant layer itself. Controlled, peelable heat seals (that  
is, openability by cohesive failure) are generally preferred  
because they offer hermetic seals which ensure product  
25 quality, tamper-evident aesthetically attractive sealant  
interface after opening as well as easy access to the  
packaged or contained product without the use of tools and  
without substantial destruction of the package or container.

The force required to peel open a package or  
30 container (that is, the defined heat strength) is tailored  
for specific end-use applications. Peelable seal sealant  
materials and formulations are used in both flexible and  
rigid container end-uses whenever easy openability and  
excellent seal integrity is required. Flexible packaging  
35 applications that utilize peelable seal sealant materials and

formulations include cereal liners, various snack food packages, cracker tubes, and cake mix liners. Peelable seal rigid packaging applications include lidding for convenience items (for example, snack foods such as puddings) and medical devices.

For flexible packaging, peelable seals generally have a defined seal strength in the range of 1 to 9 lbs./inch. For example, for easy open cereal box liners, a heat seal strength in the range of 2 to 3 lbs./inch is commonly specified, although specific targets vary according to individual manufacturer's requirements.

In addition to a defined heat seal strength to facilitate easy openability, peelable seal formulations are required to provide a low heat seal initiation temperature which helps to ensure fast packaging line speeds. Another important peelable seal sealing characteristic is a broad seal window where the defined heat seal strength is substantially constant. A broad sealing window allows packagers to compensate for packaging equipment that is not precisely tuned in terms of seal temperatures. That is, to accommodate seal jaw temperature swings or inconsistencies which is especially common for older sealing equipment. A broad sealing window is also desirable to enable high speed packaging of heat sensitive products as well as provides a degree of forgiveness respecting changes in packaging or filling speeds.

Beyond important heat seal characteristics, other important peelable seal sealant properties include excellent hot tack strength, a low coefficient of friction (COF) and good puncture resistance. Excellent hot tack strength is important for successful vertical form/fill/seal (VFFS) packaging. For the highest efficiency, the sealant layer must also provide adequate hot tack strength throughout the effective sealing window, that is, the desired level of hot tack strength must parallel the defined heat seal strength. A low COF value ensures the sealant film layer will process



smoothly and efficiently on fabrication and packaging equipment and is especially critical for vertical form/fill/seal packaging. A film-to-film kinetic COF value of less than 0.4 (especially less than 0.3) is generally required for smooth and efficient handling of sealant film layers.

An example of the need for abuse resistance and toughness is the ability of cereal box liners/sealants to withstand tears, punctures, etc. from irregularly-shaped, rigid cereals. Also, as packages are downgauged for improved economics, the abuse resistance and toughness of the sealant layer becomes all the more important. Still other important sealant layer properties (or total package/container properties) can include taste and odor performance and good barrier or transmission properties.

A common commercial structure for peelable seal cereal box liners is a coextruded HDPE/HDPE/Peelable seal sealant layer where HDPE denotes high density polyethylene. Known peelable seal compositions and sealant layer films generally include blends such as, for example, ionomer/ethylene-vinyl acetate (EVA) compositions, EVA/Polybutylene (PB) compositions, Ethylene acrylic acid (EAA) copolymer/EVA compositions, EAA/PB compositions, and even EVA/PB/polypropylene (PP) compositions. However, for flexible packaging end-uses, peelable seal sealant formulations based on an ethylene/18 weight percent vinyl acetate copolymer blended with a minor or lesser amount of a polybutylene polymer is commonly employed.

With the widespread use of polybutylene polymers for peelable seal sealant formulations, the specific characteristics, shortcomings and requirements of polybutylene formulations have become well known. In addition to use for peelable seal sealant formulations, "Polybutylene Specialty Polymers: Properties Guide," Shell Chemical Company product brochure, May 1996, the disclosure of which is incorporate herein by reference, indicates that

polybutylene homopolymers and copolymers with ethylene are supplied commercially for other end-uses, including heal sealable film applications, hot melt formulations, and polymer modifications. The product brochure indicates that polybutylene homopolymers are used (and are recommended) for hot melt formulations and as concentrate carriers and as blend components for performance and processing improvement (polymer modification). The product brochure also indicates that polybutylene copolymers having a low to medium ethylene content (that is, from 0.75 to 2 weight percent ethylene) are used (and are recommended) for peelable seal formulations.

In addition to low to medium ethylene content polybutylene copolymers, under the designations of DURAFLEX 1710 and DP 1560, Shell commercially supplies formulated products based on polybutylene resins specifically designed for blending with polyolefin polymers to prepare easy open, peelable seal sealant layers. The "Polybutylene Specialty Polymers: Properties Guide," product brochure does not specifically indicate the particular type or grade of polybutylene resin(s) employed for the specially formulated products. However, the reported typical physical properties for the specially formulated products suggest that the base resins are low-medium ethylene content polybutylene copolymers, presumably pre-blended with a minor or lesser amount of polypropylene or other olefin polymer as an incompatibilizer.

Poly(1-butene/ethylene) copolymers having a high ethylene content are also commercially available. High ethylene content polybutylene copolymers generally comprise greater than or equal to 5.5 weight percent ethylene and more typically greater than or equal to 6 weight percent ethylene copolymerized with 1-butene and are characterized by a low melting point (that is,  $\leq 90^{\circ}\text{C}$ ), low crystallinity (that is,  $< 35\text{percent}$ ), and a slow crystallization rate. The "Polybutylene Specialty Polymers: Properties Guide," product

brochure indicates that high ethylene content polybutylene copolymers are used (and are recommended) for impact modification and hot melt formulating wherein their performance characteristics of relatively long open or green times, high adhesion failure temperatures and good low temperature flex properties can be realized. Importantly, there is no disclosure or recommendation pertaining to the utility of these low crystallinity, high ethylene content polybutylene polymers for peelable seal sealant formulations.

There are a number of known polybutylene formulating issues or shortcomings related to peelable seal sealant formulations. One formulating issue relates generally to formulations based on ethylene polymers; that is, although polybutylenes are compatible in all proportions with polypropylene, they are compatible only in limited proportions with ethylene polymers. See, for example "Polybutylene Specialty Polymers: Properties Guide," at page 4. As such, when heat sealing single and multilayer sealant layers to non-polypropylene substrates, "Shell Polybutylene Resins for Easy Open Packaging," Shell Chemical Company product brochure, December 1991, the disclosure of which is incorporated herein by reference, indicates that polybutylene should be the minor component of ethylene polymer based formulations. Further, as disclosed by Mergenhagen et al. in US provisional application number 60/020,189 and also as described in "Shell Polybutylene Resins for Easy Open Packaging," at pp. 7-11, polypropylene incorporation is often used and/or recommended to compatibilize peelable seal sealant formulations comprised of ethylene polymers and polybutylene polymers.

As another shortcoming, peelable seal sealant formulations comprising polybutylene polymers are known to "age down" with time. That is, the heat seal performance (that is, seal strength) of olefin formulations based on polybutylene characteristically decrease over time. See, for example "Shell Polybutylene Resins for Easy Open Packaging,"

pp. 12-15. Depending on the blend composition, blend ratios, and fabrication techniques, heat seal strengths tend to predictably age downward 20 to 60percent. Accordingly, correlations between peel seal strengths directly off-line and aged peel seal strengths are commonly used for purposes of film quality control.

Another shortcoming pertaining generally to peelable seal sealant compositions and layers is the influence of slip additives. Slip agents and additives are routinely incorporated into peelable seal sealant formulations to reduce the coefficient of friction of the sealant film layers. However, slip additives such as fatty acid amides are known to adversely affect sealing performance by reducing ultimate seal strengths. "Shell Polybutylene Resins for Easy Open Packaging," page 12, teaches that levels of the primary fatty acid amide erucylamide (also known as erucamide) as low as 5000 ppm can cause reductions in seal strengths. Also, slip additives tend to bloom or migrate to the sealant layer surface over time and cause inconsistent sealing performance.

While known slip additive usage, problems and formulating issues suggest slip additives should be employed judiciously, slip additive use in combination with high ethylene content polybutylene/ethylene copolymers poses a particular difficulty. Specifically, due to their low crystallinities and melting points, high ethylene content polybutylene/ethylene copolymers are characteristically tacky at room temperature and, as such, require high slip additive levels to meet low COF requirements. However, high slip additive levels (for example, greater than 5000 ppm) are expected to adversely affect sealing performance. Further, since both slip additives and polybutylene characteristically alter sealing performance upon aging, any attempt to balance these adverse characteristics and provide a stable peelable seal composition and sealant layer with a defined heat seal strength, a broad sealing window and a low seal initiation

temperature appears to be contrary to known art and teachings.

De Clippeleir in "PE/PB Blends for Film Applications," Specialty Plastic Films '97, Zurich, Switzerland (December 1997), the disclosure of which is , discloses that optimum peelable seal formulating involves immiscible or incompatible polymers. De Clippeleir also discloses that linear metallocene polyethylenes (that is, homogeneously branched linear ethylene polymers such as Exxon EXACT 3132) are more compatible with polybutylene polymers than heterogeneously branched linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). Because of these differences, De Clippeleir concludes that significantly higher polybutylene polymer concentrations are needed to obtain excellent peelable seal performance with metallocene polyethylenes. De Clippeleir also concludes that polybutylene copolymers having a high ethylene content are more compatible in low density polyethylene (LDPE) than polybutylene copolymers having a low ethylene content.

In Table 2, De Clippeleir discloses a formulation consisting of 51 weight percent metallocene polyethylene, 29 weight percent polybutylene 8640 and 20 weight percent LDPE. For this low ethylene content polybutylene polymer formulation, the LDPE is said to function as an incompatibilizer and the formulation itself is described as providing excellent peelable seal and hot tack performance. Other formulation also disclosed in Table 2 (that is, 38 weight percent metallocene polyethylene, 22 weight percent polybutylene 8640 and 40 weight percent LDPE) is said to yield inconsistent peelable seal performance due to the high concentration of LDPE as an incompatibilizer. From his broad conclusions and specific showings, De Clippeleir seems to teach that if a polybutylene polymer is compatible with a particular ethylene polymer sealant base resin, then high polybutylene polymer levels and high incompatibilizer levels

are required for peelable seal formulating; however, such tend to result in inconsistent performance.

De Clippeleir does not disclose or specifically discuss any formulation consisting of a metallocene

polyethylene and a high ethylene content polybutylene polymer. Nor does De Clippeleir disclose any formulation based on a high ethylene content polybutylene polymer which provides excellent and consistent peelable seal performance.

Nor does De Clippeleir discuss COF performance for any polybutylene formulation. Moreover, from this disclosure, to prepare a formulation based on a high ethylene content polybutylene polymer and having excellent peelable seal performance, one would expect excessive quantities of the high ethylene content polybutylene polymer and/or excessive quantities of an incompatibilizer (that is, greater than a sealant base resin to incompatibilizer blend ratio of 51:20) would be required.

Although various peelable seal sealant compositions and layers are known, there nevertheless remains a need for a peelable seal, ethylene polymer sealant composition and layer which is characterized by a stable, age-resistant sealing performance wherein such performance includes a relatively low heat seal initiation temperature (that is, obtaining at least about 1.5 lbs./inch (0.27 kg/cm) heat seal strength at sealing temperatures of  $\leq 100^{\circ}\text{C}$  and 1.5-3.5 lbs./inch (0.27-0.64 kg/cm) heat seal strength at a sealing temperature of  $100^{\circ}\text{C}$ ) and a relatively broad sealing window (that is, obtaining the desired heat seal strength, for example, but not limited to, from 1.8 to 3.2 lbs./inch (0.32 to 0.57 kg/cm) of heat seal strength for cereal box liners, in a sealing temperature range of  $\geq 20^{\circ}\text{C}$ ). There also remains a need for peelable seal sealant layer characterized by a stable, age-resistant reduced coefficient of friction characteristic (that is, a film-to-film COF less than or equal to 0.3). There is also a need for a peelable seal sealant layer with sealing performance comparable to

incumbent EVA/polybutylene formulations without the characteristic off-taste of such formulations. These and other objects can be met by the present invention as described herein below.

We have discovered a novel sealant composition and layer which is comprised a plurality of olefin polymers and slip and silica-containing or calcium-containing additives. In preferred embodiments, the sealant layer is characterized as having an age-resistant easy-to-open heat seal characteristic, a broad sealing window, a low seal initiation temperature, exceptional hot tack performance which parallels heat seal performance and a low COF. The broad aspect of the present invention is a peelable seal sealant composition comprising

- a) as a sealant base resin, at least one ethylene polymer,
- b) at least 25 weight percent, based on the total weight of the composition, of at least one polybutylene polymer,
- c) greater than 0.5 weight percent, based on the total weight of the composition, of at least one slip additive, and
- d) at least 0.5 weight percent, based on the total weight of the composition, of at least one silica-containing or calcium-containing additive,

wherein the composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as having:

- (i) a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

(ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

5 wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.277 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25.4 cm/minute).

10 One preferred aspect of the present invention is a sealant composition comprising

a) as a sealant base resin, at least one homogeneously branched ethylene polymer characterized by a lack of a polymer fraction having a degree of short chain  
15 branching less than or equal to 2 methyls/1000 carbons and greater than or equal to 30 methyls/1000 carbons, as determined using a temperature rising elution fractionation and infrared (IR) technique,

b) at least 25 weight percent, based on the  
20 total weight of the composition, of at least one polybutylene polymer having a crystallinity less than 36 weight percent, based on the total weight of the polymer, as determined using wide-angle X ray,

c) greater than 0.5 weight percent, based on  
25 the total weight of the composition, of at least one slip additive, and

d) at least 0.5 weight percent, based on the total weight of the composition, of at least one silica-containing or calcium-containing additive,

30 wherein the composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as having:

(i) a heat seal initiation performance, wherein after the layer is aged  
35 for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer



has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm)

width at a sealing temperature of 100°C, and

(ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C.

Preferably, the inventive composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as having (iii) a heat seal strength average deviation of less than or equal to 16.5 percent for sealing temperatures from 100° to 130°C.

More preferably, the inventive composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil, is characterized as having a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.6 to 3.2 lbs./inch (0.32 to 0.57 kg/cm) at a sealing temperature of 90°C.

Most preferably, the inventive composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is further characterized as maintaining the (iii) characteristic after aging at 22-23°C and 50 percent relative humidity for 528 hours (22 days) following fabrication of the layer.

For this aspect of the invention, heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.277 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25.4 cm/minute).

In one specifically preferred embodiment, the inventive composition is characterized as having a heat

sealing window plateau of greater than or equal to 20°C,  
preferably greater than or equal to 25°C, more preferably  
greater than or equal to 30°C and most preferably greater than  
or equal to 35°C for a defined heat seal strength of about 1.8  
5 to 3.2 lbs./inch when fabricated into a sealant layer having  
a thickness of from 0.28 to 0.3 mil and thereafter aged at  
22-23°C and 50 percent relative humidity for at least 528  
hours following fabrication of the layer.

Another aspect of the present invention is a film  
10 having at least one sealant layer, the at least one sealant  
layer comprising

a) as a sealant base resin, at least one  
homogeneously branched ethylene polymer characterized by a  
lack of a polymer fraction having a degree of short chain  
15 branching less than or equal to 2 methyls/1000 carbons and  
greater than or equal to 30 methyls/1000 carbons, as  
determined using a temperature rising elution fractionation  
and infrared (IR) technique,

b) at least 25 weight percent, based on the  
20 total weight of the layer, of at least one polybutylene  
polymer having a crystallinity less than 36 weight percent,  
based on the total weight of the polymer, as determined using  
wide-angle X ray,

c) greater than 0.5 weight percent, based on  
25 the total weight of the layer, of at least one slip additive,  
and

d) at least 0.5 weight percent, based on the  
total weight of the layer, of at least one silica-containing  
or calcium-containing additive,

30 wherein the sealant layer at a thickness of from  
0.28 to 0.3 mil is characterized as having:

(i) a heat seal initiation  
performance, wherein after the layer is aged  
for less than or equal to 192 hours at 22-23°C  
35 and 50 percent relative humidity, the layer

has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

(ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.277 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute.

Another aspect of the present invention is a method for making a peelable seal film or coating structure having at least two layers, the method comprising the steps of:

(i) feeding a first polymer composition into a sealant layer coextrusion extruder,

(ii) feeding a second polymer composition into a skin layer coextrusion extruder,

(iii) optionally feeding a polymer composition into a core or structural layer coextrusion extruder,

(iv) melting and mixing the polymer compositions at melt temperatures above their melting points to form at least two molten polymer streams,

(vi) extruding the molten polymer streams through a coextrusion feedblock into a die to form a web or a tube comprising a sealant layer and a skin layer,

(vii) blowing up and cooling the tube or drawing down and cooling the web to form the peelable seal film or coating structure, and

(viii) collecting the film or coating

structure,

the method wherein the first polymer composition comprises

5           a)           as a sealant base resin, at least one homogeneously branched ethylene polymer characterized by a lack of a polymer fraction having a degree of short chain branching less than or equal to 2 methyls/1000 carbons and greater than or equal to 30 methyls/1000 carbons , as

10           determined using a temperature rising elution fractionation and infrared (IR) technique,

          b)           at least 25 weight percent, based on the total weight of the composition, of at least one polybutylene polymer having a crystallinity less than 36 weight percent, 15           based on the total weight of the polymer, as determined using wide-angle X ray,

          c)           greater than 0.5 weight percent, based on the total weight of the composition, of at least one slip additive, and

20           d)           at least 0.5 weight percent, based on the total weight of the composition, of at least one silica-containing or calcium-containing additive,

          wherein the first polymer composition, when fabricated into a sealant layer having a thickness of from 25           0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as having:

          (ix) a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer 30           has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

          (x) a median heat seal strength in 35           the range of from 2.6 to 4.0 lbs./inch (0.46

to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.277 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25.4 cm/minute).

A fourth aspect of the present invention is a film or coated structure comprising at least one sealant layer and at least one additional film layer wherein the additional film layer is selected from the group consisting of a polyamide, polyethylene, polypropylene, polyester, polyvinylidene chloride and polycarbonate and the sealant layer comprises

a) as a sealant base resin, at least one homogeneously branched ethylene polymer characterized by a lack of a polymer fraction having a degree of short chain branching less than or equal to 2 methyls/1000 carbons and greater than or equal to 30 methyls/1000 carbons, as determined using a temperature rising elution fractionation and infrared (IR) technique,

b) at least 25 weight percent, based on the total weight of the layer, of at least one polybutylene polymer having a crystallinity less than 36 weight percent, based on the total weight of the polymer, as determined using wide-angle X ray,

c) greater than 0.5 weight percent, based on the total weight of the layer, of at least one slip additive, and

d) at least 0.5 weight percent, based on the total weight of the layer, of at least one silica-containing or calcium-containing additive,

wherein the sealant layer at a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm) is characterized as having:

(i) a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

(ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25.4 cm/minute).

The composition, first polymer composition and sealant layer of the present invention exhibit peelable seal performance characterized by defined heat seal strengths within a narrow heat seal strength range or width (that is, has a heat seal strength average deviation of less than or equal to 16.5 percent) as well as by broad heat sealing window plateaus (for example, greater than or equal to 20°C at a defined heat seal strength of from 1.8 to 3.2 lbs./inch (0.32 to 0.57 kg/cm)).

As one of the significant surprises of the invention, we discovered that it is possible to provide a peelable seal sealant composition characterized by relatively smooth and uniform sealing window plateaus across a broad temperature range at relatively high levels of a polybutylene polymer without the use of ternary polymer blends or the addition of an incompatibilizing olefin polymer such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE) or polypropylene. For example, in the present invention, neither low density polyethylene (LDPE) nor

polypropylene is required as an incompatibilizer for the inventive composition based on at least one homogeneously branched ethylene polymer (and vice versa). However, in specific embodiments, surprisingly the inventive compositions comprises relatively high levels of an ethylene polymer as an incompatibilizer and still exhibits excellent peelable seal performance and exceptional consistency when aged up to at least 14 days.

As another surprise, we also discovered that at relatively high levels, the at least one polybutylene polymer provides an unexpected improvement respecting heat seal initiation temperatures. That is, while polybutylene polymers are expected to increase heat seal initiation temperatures at high levels (and in fact do so at level of 0-25 weight percent based on the total weight of the composition), in the present invention, we surprisingly discovered that the use of least one polybutylene polymer having a relatively low crystallinity at the specified levels of the invention discontinues the expected trend of increasing heat seal initiation temperatures as function of higher polybutylene polymer levels. Instead of having a relatively high heat seal initiation temperature as expected, the present composition and sealant layer have a relatively low heat seal initiation temperature in that heat seal strengths in the range of 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width are obtained at 100°C.

A third surprise of the invention is its characteristic stable, age-resistant sealing performance even though relatively high levels of at least one polybutylene copolymer and, more surprisingly, relatively high levels of at least one slip additives are employed. Ordinarily high levels of polybutylene polymers and slip additives (such as, for example, fatty acid amides) are expected to adversely affect or at least substantially alter sealing characteristics and performance. For specific embodiments, no such adverse effects or substantial variations occur for

the inventive composition when aged 22 days and, even more surprisingly, 37 days following film fabrication.

An important advantage of the invention is now an olefin based peelable seal sealant composition and layer is available for flexible and rigid packaging applications that exhibits excellent and consistent sealing performance without the off-taste characteristics typically associated with formulations based on an 18percent vinyl acetate EVA copolymer blended with a polybutylene polymer.

FIG. 1 is a graphical illustration of heat sealing characteristics which includes initiation temperature, defined heat seal strength and sealing window.

FIG. 2 is a plot of sealing temperature versus the initial heat seal strength (sealing profile) for Inventive Examples 1, 2 and 8 and comparative examples 3, 4, 5, 6, and 7. The initial heat strength was taken for seals made and pulled eight days after film fabrication.

FIG. 3 is a plot of sealing temperature versus the 22-day aged heat seal strength for Inventive Examples 1, 2 and 8 and comparative examples 3, 4, 5, 6, and 7. The 22-day aged heat strength was taken for seals made and pulled 22 days after film fabrication.

FIG. 4 is a plot of sealing temperature versus the 37-day aged heat seal strength for Inventive Examples 1, 2 and 8 and comparative examples 3, 4, 5, 6, and 7. The 37-day aged heat strength was taken for seals made and pulled 37 days after film fabrication.

FIG. 5 is a plot of heat seal strength at 90°C versus weight percent polybutylene polymer (Shell DP8310) for Inventive Examples 1, 2 and 8 and comparative 3-7 aged 8 days, 22 days and 37 days.

FIG. 6 is a plot of heat seal strength at 100°C versus weight percent polybutylene polymer (Shell DP8310) for Inventive Examples 1, 2 and 8 and comparative 3-7 aged 8 days, 22 days and 37 days.



FIG. 7 is a plot of sealing temperature versus the initial 8-day hot tack strength for Inventive Examples 1, 2 and 8 and comparative examples 3, 4, 5, 6, and 7. The initial hot tack strength was taken for seals made 8 days after film fabrication.

FIG. 8 is a plot of sealing temperature versus the 22-day hot tack strength for Inventive Examples 1, 2 and 8 and comparative examples 3, 4, 5, 6, and 7. The 22-day hot tack strength was taken 22 days after film fabrication.

FIG. 9 is a plot of sealing temperature versus the 37-day hot tack strength for Inventive Examples 1, 2 and 8 and comparative examples 3, 4, 5, 6, and 7. The 37-day hot tack strength was taken 37 days after film fabrication.

FIG. 10 is a plot of polybutylene polymer density and ethylene content versus weight percent crystallinity as determined by wide-angle X ray analysis.

FIG. 11 a plot illustrating the heat seal profiles of comparative examples 9-12.

FIG. 12 a plot illustrating the hot tack profiles of comparative examples 9-11.

FIG. 13 a bar chart illustrating the clarity comparison between comparative examples 9-11.

FIG. 14 a bar chart illustrating the percent haze comparison between comparative examples 9-11.

FIG. 15 a bar chart illustrating the puncture resistance comparison between comparative examples 9-11.

FIG. 16 a bar chart illustrating the sealant-to-metal (outside film-to-metal) COF comparison between comparative examples 9-11.

FIG. 17 a bar chart illustrating the sealant-to-sealant (outside film-to-outside film) COF comparison between comparative examples 9-11.

FIG. 18 a plot illustrating the heat seal profiles of Inventive Examples 14, 15, 16, 17, 19 and 20 and comparative examples 18 and 21.

FIG. 19 a plot illustrating the heat seal profiles of Inventive Example 16 and comparative examples 21, 22 and 23.

FIG. 20 a plot illustrating the sealant-to-sealant (outside film-to-outside film) COF comparison between Inventive Examples 14, 15 and 16 comparative example 18.

FIG. 21 is a plot of ethylene polymer density versus weight percent crystallinity as determined using DSC.

The term "blow-up ratio" (abbreviated "BUR"), as used herein, means the ratio of the blown film bubble diameter to the blown film unit die diameter.

The term "drawdown ratio" as used herein, means the ratio of machine direction to cross direction stretching or elongating a molten polymer extrudate (web or filament).

The term "slip additive" as used herein refers to a compound (for example fatty acid amides) which improves the coefficient of friction (COF) of a film or coating layer (that is reduces the film-to-film kinetic COF to less than or equal to 0.4 as determined in accordance with ASTM D1894,). The terms "slip additive" and "silica-containing or calcium-containing additive" refer to the additive or compound itself and excludes carrier resin.

The term "polymer", as used herein, refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. As used herein, generic term "polymer" embraces the terms "homopolymer," "copolymer," "terpolymer" as well as "interpolymer."

The term "interpolymer", as used herein refers to polymers prepared by the polymerization of at least two different types of monomers. As used herein the generic term "interpolymer" includes the term "copolymers" (which is usually employed to refer to polymers prepared from two different monomers) as well as the term "terpolymers" (which is usually employed to refer to polymers prepared from three different types of monomers).

The term "non-polar" is used herein in its conventional sense to refer to ethylene polymers which do not contain monomers or comonomers having a polar moiety such as the case for ethylene vinyl acetate (EVA) copolymers and  
5 ethylene acrylic acid (EAA) copolymers.

FIG. 1 graphically illustrates the desired heat sealing profile for a peelable seal sealant material as compared to other sealant materials depicted as having a poor or objectionable sealing characteristics. The figure shows a  
10 defined heat seal strength of 1.8-3.2 lbs./inch (0.27 to 0.639 kg/cm) which provides a median or target heat seal strength of 2.5 lbs./inch (0.45 kg/cm), a low seal initiation temperature at about 73°C and a broad sealing window (that is, the temperature range of from 74.5°C to 154°C provides a  
15 sealing window or plateau of about 79.5°C wherein the defined heat seal strength of 1.8-3.2 lbs./inch (0.27 to 0.639 kg/cm) can be obtained). The sealing window is also depicted as having an absolute range of 28 percent or  $\pm 0.7$  lbs./inch (0.13 kg/cm) (that is,  $3.2 \div 2.5 \times 100$  or  $3.2 - 2.5$ ,  
20 respectively) and an average deviation of zero in the sealing temperature range of 90°-140°C.

In the present invention, sealing consistency (that is, the flatness of sealing window plateaus initially and upon aging) is expressed in terms of percent average  
25 deviation throughout the sealing temperature range of 100°-130°C or, alternatively, 90°-140°C, as determined by computing specific heat seal strength data with respect to sealing temperatures corresponding to a heat sealer. The term  
30 "average deviation" is used herein in the conventional sense to refer to the statistical computation which provides the average of the absolute deviations of data points from their mean as a measure of the variability in the data set. In the present invention, the average deviation is determined according to the following equation:

$$\frac{1}{n} \sum x - \bar{x}$$

where  $n$  is the number of data points in a data set and is at least 6;  $x$  is the heat seal strength value (in lbs./inch) for a specific sealing temperature (for example, 90°, 95°, 100°, 110°, 105°, 115°, 120°, 125°, 130° and 140°C); and  $\bar{x}$  is the average or mean heat seal strength (in lbs./inch) of the data set. Also, the computation always includes heat seal strength values at the endpoint temperatures of the range, that is, 100°C and 130°C or, alternatively, 90°C and 140°C. To express average deviation as a percentage, the computed average deviation is divided by the median heat seal strength (not the mean or average heat seal strength as is the case for  $\bar{x}$ ) for the prescribed temperature range and multiplied by 100.

The same computation can be used to determine the average deviation for hot tack strength data, although hot tack data in particular tends to vary widely. Characterization of sealing performance in terms average deviation is preferred because the computation is independent of the specific defined heat seal strength (or hot tack strength) required for a particular end-use and the computation conveniently distinguishes aged and unaged sealant layers on the basis of performance variability.

As an example of a heat seal strength/sealing window average deviation computation, where a sealant layer measures heat seal strengths of 1.8 lbs./inch (0.32 kg/cm) at 90°C; 2.0 lbs./inch (0.36 kg/cm) at 95°C; 2.2 lbs./inch (0.39 kg/cm) at 100°C; 2.4 lbs./inch (0.43 kg/cm) at 105°C; 2.5 lbs./inch (0.45 kg/cm) at 110°C; 2.5 lbs./inch (0.45 kg/cm) at 115°C; 2.6 lbs./inch (0.46 kg/cm) at 120°C; 2.8 lbs./inch (0.5 kg/cm) at 125°C; 3.0 lbs./inch (0.54 kg/cm) at 130°C; and 3.2 lbs./inch (0.57 kg/cm) at 140°C,  $n$  equals 9, the median heat seal strength is 2.5 lbs./inch (0.45 kg/cm), the average deviation of the heat seal strengths is 0.32 lbs./inch (0.06

kg/cm) or 13 percent while the absolute range for the sealing window in the temperature range of 90°-140°C is 28 percent. The inventive composition when fabricated as sealant layer having a thickness of from 0.28 to 0.3 mil is characterized as having a heat seal strength average deviation of less than or equal to 16.5 percent, preferably less than or equal to 12 percent, more preferably less than or equal to 9 percent and most preferably less than or equal to 6 percent for the sealing temperature range of 100°-130°C. More especially, the sealant layer at a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm) is characterized as having a heat seal strength average deviation of less than or equal to 22 percent, preferably less than or equal to 17 percent, more preferably less than or equal to 13 percent and most preferably less than or equal to 11.5 percent for the sealing temperature range of 90°-140°C.

The sealing window plateau and absolute range for a sealant layer are specific with respect to a defined heat seal strength. The term "absolute range" is used herein as a percentage to denote to the computation derived by dividing the upper heat seal strength of a defined heat seal strength by the median heat strength of the defined heat seal strength and multiplying the product by 100. The term "sealing window plateau" is used herein to refer to the sealing temperature spread (in °C) wherein a sealant layer measures heat seal strengths within a defined heat seal strength.

As defined by the present invention, the combination of at least one ethylene polymer with (1) at least 25 weight percent of at least one polybutylene polymer, (2) greater than 0.5 weight percent of at least one slip additive, and (3) at least 0.5 weight percent of at least one silica-containing or calcium-containing additive exhibits improved peelable seal behavior. Specific blend ratios or component weight percentages within the limits specified by invention can be chosen to reach a target peel strength based

on the seal performance requirements for a specific application. However, preferably the weight percent of the at least one ethylene polymer (sealant base resin) will be from 25 to 73 weight percent, based on the total weight of the inventive composition, more preferably from 30 to 70 weight percent, based on the total weight of the inventive composition, most preferably from 32 to 67 weight percent, based on the total weight of the inventive composition and especially from 36 to 46 weight percent, based on the total weight of the inventive composition.

Ethylene polymers for use in the invention are preferably non-polar ethylene homopolymers and interpolymers such as low density polyethylene (LDPE), heterogeneously branched ethylene/ $\alpha$ -olefin interpolymer (that is, linear low density polyethylene (LLDPE) and ultra low density polyethylene (ULDPE)) and homogeneously branched ethylene polymer. However, the most preferred ethylene polymers for use in the invention as the at least one ethylene polymer sealant base resin are homogeneously branched ethylene polymers.

Generally, the weight percent of the at least one polybutylene copolymer is greater than 25 weight percent, based on the total weight of the composition, preferably from 27 to 73 weight percent, based on the total weight of the composition, and more preferably from 27 to 58 weight percent, based on the total weight of the composition, most preferably from 30 to 47 weight percent, based on the total weight of the composition, and especially from 32 to 44 weight percent, based on the total weight of the composition.

Generally, the weight percent of the at least one slip additive will be greater than 0.56 weight percent (that is, > 6000 parts per million (ppm)), based on the total weight of the composition, preferably from 0.7 weight percent to 1.5 weight percent, based on the total weight of the composition, and more preferably from 0.8 to 1.2 weight percent, based on the total weight of the composition.

Generally, the weight percent of at least one silica-containing or calcium-containing additive will be at least 0.5 weight percent (that is,  $\geq 5000$  ppm), based on the total weight of the composition), preferably from 0.5 weight percent to 10 weight percent, based on the total weight of the composition, more preferably from 0.7 to 1.8 weight percent, based on the total weight of the composition and most preferably from 0.8 to 1.2 weight percent, based on the total weight of the composition.

The term "homogeneously branched ethylene polymer" is used herein in the conventional sense to refer to an ethylene interpolymer in which the comonomer is randomly distributed within a given polymer molecule and wherein substantially all of the polymer molecules have the same ethylene to comonomer molar ratio. The term refers to an ethylene interpolymer that is characterized by a relatively high short chain branching distribution index (SCBDI) or composition distribution branching index (CDBI). That is, the interpolymer has a SCBDI greater than or equal to 50 percent, preferably greater than or equal to 70 percent, more preferably greater than or equal to 90 percent. Preferably, the homogeneously branched ethylene polymer is defined as having a narrow, essentially single melting TREF profile/curve and essentially lacking a measurable high density polymer portion (that is the polymer does not contain a polymer fraction with a degree of short chain branching less than or equal to 2 methyls/1000 carbons nor equal to or greater than 30 methyls/1000 carbons or, alternatively, at densities less than 0.936 g/cc, the polymer does not contain a polymer fraction eluting at temperatures greater than 95°C). as determined using a temperature rising elution fractionation technique (abbreviated herein as "TREF").

SCBDI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content and represents a comparison of the monomer distribution in the

interpolymer to the monomer distribution expected for a Bernoullian distribution. The SCBDI of an interpolymer can be readily calculated from TREF as described, for example, by Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in US Patent 4,798,081; 5,008,204; or by L. D. Cady, "The Role of Comonomer Type and Distribution in LLDPE Product Performance," SPE Regional Technical Conference, Quaker Square Hilton, Akron, Ohio, October 1-2, pp. 107-119 (1985), the disclosures of all which are incorporated herein by reference. However, the preferred TREF technique does not include purge quantities in SCBDI calculations. More preferably, the monomer distribution of the interpolymer and SCBDI are determined using  $^{13}\text{C}$  NMR analysis in accordance with techniques described in US Patent No. 5,292,845; US Patent No. 4,798,081; U.S. Patent No. 5,089,321 and by J. C. Randall, Rev. Macromol. Chem. Phys., C29, pp. 201-317.

In analytical temperature rising elution fractionation analysis (as described in US Patent No. 4,798,081 and abbreviated herein as "ATREF"), the film or composition to be analyzed is dissolved in a suitable hot solvent (for example, trichlorobenzene) and allowed to crystallized in a column containing an inert support (stainless steel shot) by slowly reducing the temperature. The column is equipped with both a refractive index detector and a differential viscometer (DV) detector. An ATREF-DV chromatogram curve is then generated by eluting the crystallized polymer sample from the column by slowly increasing the temperature of the eluting solvent (trichlorobenzene). The ATREF curve is also frequently called the short chain branching distribution (SCBD), since it indicates how evenly the comonomer (for example, octene) is distributed throughout the sample in that as elution temperature decreases, comonomer content increases. The refractive index detector provides the short chain distribution information and the differential viscometer



detector provides an estimate of the viscosity average molecular weight. The short chain branching distribution and other compositional information can also be determined using crystallization analysis fractionation such as the CRYSTAF  
5 fractionanalysis package available commercially from PolymerChar, Valencia, Spain.

The homogeneously branched ethylene polymers for use in the invention can be a homogeneously branched substantially linear ethylene interpolymer or a homogeneously  
10 branched linear ethylene polymer. The homogeneously branched ethylene polymer can optionally be blended with at least one other ethylene polymer to provide the at least one sealant base resin or a sealant polymer blend. Suitable polymers for blending with homogeneously branched ethylene polymers  
15 include, for example, a low density polyethylene homopolymer, substantially linear ethylene polymers, homogeneously branched linear ethylene polymers, heterogeneously branched linear ethylene polymers (that is, linear low density polyethylene (LLDPE), ultra or very low density polyethylene  
20 (ULDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE) such as those manufactured using a Ziegler-Natta catalyst system).

Preferably, the homogeneously branched ethylene polymer is characterized as having a single DSC melt point in  
25 the temperature range from -30°C to 150°C. More preferably, the at least one homogeneously branched ethylene polymers, like all homogeneously branched substantially linear ethylene polymers, are further characterized as having a single DSC melting peak in the range of from -30°C to 150°C and  
30 consisting of a single polymer component material. Most preferably, the homogeneously branched ethylene polymer is a homogeneously branched substantially linear ethylene interpolymer.

Homogeneously branched substantially linear  
35 ethylene polymers are sold under the designation of AFFINITY™ and ENGAGE™ resins by The Dow Chemical Company and Dupont Dow

Elastomers, respectively. Homogeneously branched linear ethylene polymers are sold under the designation of TAFMER by Mitsui Chemical Corporation and under the designations of EXACT and EXCEED resins by Exxon Chemical Corporation.

5 In addition to referring to a homogeneous (or narrow) short branching distribution, the term "homogeneously branched linear ethylene polymer" also means the interpolymer does not have long chain branching. That is, the ethylene interpolymer has an absence of long chain branching and a  
10 linear polymer backbone in the conventional sense of the term "linear." However, the term "homogeneously branched linear ethylene polymer" does not refer to high pressure branched polyethylene which is known to those skilled in the art to have numerous long chain branches.

15 Homogeneously branched linear ethylene polymers can be made using polymerization processes (for example, those described by Elston in USP 3,645,992, the disclosure of which is incorporated herein by reference) which provide a uniform (narrow) short branching distribution (that is, homogeneously  
20 branched). In his polymerization process, Elston uses soluble vanadium catalyst systems to make such polymers, however others such as Mitsui Chemical Corporation and Exxon Chemical Corporation have used so-called single site catalyst systems to make polymers having a similar homogeneous  
25 structure. Homogeneously branched linear ethylene polymers can be prepared in solution, slurry or gas phase processes using hafnium, zirconium and vanadium catalyst systems. Ewen et al. in U.S. Pat. No. 4,937,299 describe a method of preparation using metallocene catalysts. The disclosures of  
30 Elston and Ewen et al. are incorporated herein by reference.

Typically, the homogeneously branched linear ethylene polymers are ethylene/ $\alpha$ -olefin interpolymers, wherein the  $\alpha$ -olefin is at least one C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -olefin (for example, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene,  
35 1-hexene, heptene and 1-octene) and preferably the at least one C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -olefin is 1-butene, 1-hexene, heptene or 1-

octene. Most preferably, the ethylene/ $\alpha$ -olefin interpolymer is a copolymer of ethylene and a  $C_3$ - $C_{20}$   $\alpha$ -olefin, and especially an ethylene/ $C_4$ - $C_8$   $\alpha$ -olefin copolymer such as an ethylene/1-octene copolymer, ethylene/1-butene copolymer, ethylene/1-pentene copolymer or ethylene/1-hexene copolymer.

The term "substantially linear ethylene polymer" as used herein means that the bulk ethylene polymer is substituted, on average, with 0.01 long chain branches/1000 total carbons to 3 long chain branches/1000 total carbons (wherein "total carbons" includes both backbone and branch carbons). Preferred polymers are substituted with 0.01 long chain branches/1000 total carbons to 1 long chain branches/1000 total carbons, more preferably from 0.05 long chain branches/1000 total carbons to 1 long chain branched/1000 total carbons, and especially from 0.3 long chain branches/1000 total carbons to 1 long chain branches/1000 total carbons.

As used herein, the term "backbone" refers to a discrete molecule, and the term "polymer" or "bulk polymer" refers, in the conventional sense, to the polymer as formed in a reactor. For the polymer to be a "substantially linear ethylene polymer", the polymer must have at least enough molecules with long chain branching such that the average long chain branching in the bulk polymer is at least an average of from 0.01/1000 total carbons to 3 long chain branches/1000 total carbons.

The term "bulk polymer" as used herein means the polymer which results from the polymerization process as a mixture of polymer molecules and, for substantially linear ethylene polymers, includes molecules having an absence of long chain branching as well as molecules having long chain branching. Thus a "bulk polymer" includes all molecules formed during polymerization. It is understood that, for the substantially linear polymers, not all molecules have long chain branching, but a sufficient amount do such that the average long chain branching content of the bulk polymer

positively affects the melt rheology (that is, the melt fracture properties) as described herein below and elsewhere in the literature.

Long chain branching (LCB) is defined herein as a chain length of at least one (1) carbon less than the number of carbons in the comonomer, whereas short chain branching (SCB) is defined herein as a chain length of the same number of carbons in the residue of the comonomer after it is incorporated into the polymer molecule backbone. For example, a substantially linear ethylene/1-octene polymer has backbones with long chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

Long chain branching can be distinguished from short chain branching by using  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy and to a limited extent, for example for ethylene homopolymers, it can be quantified using the method of Randall, (Rev. Macromol.Chem. Phys., C29 (2&3), p. 285-297). However as a practical matter, current  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of about six (6) carbon atoms and as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch. The long chain branch can be as long as about the same length as the length of the polymer backbone.

Although conventional  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of six carbon atoms, there are other known techniques useful for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. For example, US Patent No. 4,500,648, incorporated herein by reference, teaches that long chain branching frequency (LCB) can be represented by the equation  $\text{LCB} = b/M_w$  wherein  $b$  is the weight average number of long chain branches per molecule and  $M_w$  is the weight

average molecular weight. The molecular weight averages and the long chain branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods, respectively.

5 Two other useful methods for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation  
10 chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, for example, Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949)  
15 and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the October 4, 1994 conference of the Federation of Analytical Chemistry and Spectroscopy  
20 Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is a useful technique for quantifying the presence of long chain branches in substantially linear ethylene polymers. In particular, deGroot and Chum found that the level of long chain branches  
25 in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using  $^{13}\text{C}$  NMR.

Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the  
30 polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short  
35 chain branches, deGroot and Chum showed that GPC-DV may be

used to quantify the level of long chain branches in substantially linear ethylene/octene copolymers.

DeGroot and Chum also showed that a plot of Log( $I_2$ , melt index) as a function of Log(GPC Weight Average Molecular Weight) as determined by GPC-DV illustrates that the long chain branching aspects (but not the extent of long branching) of substantially linear ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

For substantially linear ethylene polymers, the long chain branch is longer than the short chain branch that results from the incorporation of the  $\alpha$ -olefin(s) into the polymer backbone. The empirical effect of the presence of long chain branching in the substantially linear ethylene polymers used in the invention is manifested as enhanced rheological properties which are quantified and expressed herein in terms of gas extrusion rheometry (GER) results and/or melt flow,  $I_{10}/I_2$ , increases.

The substantially linear ethylene polymers used in the present invention are a unique class of compounds that are further defined in US Patent 5,272,236, serial number 07/776,130, filed October 15, 1991, and in US patent 5,278,272, serial number 07/939,281, filed September 2, 1992.

Substantially linear ethylene polymers differ significantly from the class of polymers conventionally known as homogeneously branched linear ethylene polymers described above and, for example, by Elston in US Patent 3,645,992. As an important distinction, substantially linear ethylene polymers do not have a linear polymer backbone in the conventional sense of the term "linear" as is the case for homogeneously branched linear ethylene polymers.

Substantially linear ethylene polymers also differ significantly from the class of polymers known conventionally

as heterogeneously branched traditional Ziegler polymerized linear ethylene interpolymers (for example, ultra low density polyethylene, linear low density polyethylene or high density polyethylene made, for example, using the technique disclosed by Anderson et al. in US Patent 4,076,698, in that substantially linear ethylene interpolymers are homogeneously branched polymers; that is, substantially linear ethylene polymers have a SCBDI greater than or equal to 50 percent, preferably greater than or equal to 70 percent, more preferably greater than or equal to 90 percent.

Substantially linear ethylene polymers also differ from the class of heterogeneously branched ethylene polymers in that substantially linear ethylene polymers are characterized as essentially lacking a measurable high density or crystalline polymer fraction as determined using a temperature rising elution fractionation technique.

Substantially linear ethylene polymers also differ significantly from the class of polymers known as free-radical initiated, highly branched high pressure low density ethylene homopolymer and ethylene interpolymers such as, for example, ethylene-acrylic acid (EAA) copolymers and ethylene-vinyl acetate (EVA) copolymers. That is, substantially linear ethylene polymers do not have equivalent degrees of long chain branching as high pressure, free-radical initiated ethylene polymers and are made using single site catalyst systems rather than free-radical peroxide catalysts systems.

Metallocene single site polymerization catalyst, (for example, the monocyclo-pentadienyl transition metal olefin polymerization catalysts described by Canich in US Patent 5,026,798 or by Canich in US Patent 5,055,438) or constrained geometry catalysts (for example, as described by Stevens et al. in US Patent 5,064,802) can be used to manufacture substantially linear ethylene polymers, so long as the manufacture and metallocene catalyst system are used consistent with the methods described in US Patent 5,272,236 and in US Patent 5,278,272. Such polymerization methods are

also described in PCT/US 92/08812 (filed October 15, 1992). However, the substantially linear ethylene polymers are preferably manufactured using suitable constrained geometry catalysts, especially constrained geometry catalysts as disclosed in US Application Serial Nos.: 545,403, filed July 3, 1990; U.S. Pat. No. 5,132,380; U.S. Pat. No. 5,064,802; U.S. Pat. No. 5,153,157; U.S. Pat. No. 5,470,993; U.S. Pat. No. 5,453,410; U.S. Pat. No. 5,374,696; U.S. Pat. No. 5,532,394; U.S. Pat. No. 5,494,874; and U.S. Pat. No. 5,189,192.

Suitable cocatalysts for use herein include but are not limited to, for example, polymeric or oligomeric aluminoxanes, especially methyl aluminoxane or modified methyl aluminoxane (made, for example, as described in US Patent 5,041,584, US Patent 4,544,762, US Patent 5,015,749, and/or US Patent 5,041,585) as well as inert, compatible, non-coordinating, ion forming compounds. Preferred cocatalysts are inert, non-coordinating, boron compounds.

Homogeneously branched substantially linear ethylene polymers can be prepared via the continuous solution, slurry, or gas phase polymerization of ethylene and at least one optional  $\alpha$ -olefin comonomer in the presence of a constrained geometry catalyst, such as the method disclosed in European Patent Application 416,815-A, which is incorporated herein by reference. The polymerization can generally be performed in any reactor system known in the art including, but not limited to, a tank reactor(s), a sphere reactor(s), a recycling loop reactor(s) or combinations thereof, any reactor or all reactors operated partially or completely adiabatically, nonadiabatically or a combination of both. Preferably, a continuous solution polymerization process is used to manufacture the substantially linear ethylene polymer used in the present invention.

The substantially linear ethylene polymer for use in the present invention is characterized as having

(a) melt flow ratio,  $I_{10}/I_2 \geq 5.63$ ,



(b) a molecular weight distribution,  $M_w/M_n$ , as determined by gel permeation chromatography and defined by the equation:

$$(M_w/M_n) \leq (I_{10}/I_2) - 4.63,$$

5 (c) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt  
10 fracture for a linear ethylene polymer, wherein the substantially linear ethylene polymer and the linear ethylene polymer comprise the same comonomer or comonomers, the linear ethylene polymer has an  $I_2$  and  $M_w/M_n$  within ten percent of the  
15 substantially linear ethylene polymer and wherein the respective critical shear rates of the substantially linear ethylene polymer and the linear ethylene polymer are measured at the same melt temperature using a gas extrusion rheometer,  
20 and

(d) a single differential scanning calorimetry, DSC, melting peak between  
-30° and 150°C.

The substantially linear ethylene interpolymers  
25 used in the present invention are interpolymers of ethylene with at least one  $C_3$ - $C_{20}$   $\alpha$ -olefin and/or  $C_4$ - $C_{18}$  diolefin. Copolymers of ethylene and an  $\alpha$ -olefin of  $C_3$ - $C_{20}$  carbon atoms are especially preferred. The term "interpolymer" as  
discussed above is used herein to indicate a copolymer, or a  
30 terpolymer, or the like, where, at least one other comonomer is polymerized with ethylene or propylene to make the interpolymer.

Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example,  
35 ethylenically unsaturated monomers, conjugated or non-

conjugated dienes, polyenes, etc. Examples of such comonomers include C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -olefins such as propylene, isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, .

5 Preferred comonomers include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, heptene and 1-octene, and 1-octene is especially preferred. Other suitable monomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene,  
10 1,7-octadiene, and cycloalkenes, for example, cyclopentene, cyclohexene and cyclooctene.

Determination of the critical shear rate and critical shear stress in regards to melt fracture as well as other rheology properties such as "rheological processing  
15 index" (PI), is performed using a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, No. 11, p. 770 (1977) and in Rheometers for Molten  
20 Plastics by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99, the disclosures of both of which are incorporated herein by reference. GER experiments are performed at a temperature of about 190°C, at nitrogen pressures between 250 to 5500 psig (1.7 to 37.9 MPa) using a  
25 0.0754 mm diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of about  $2.15 \times 10^6$  dyne/cm<sup>2</sup> (2150 MPa). The substantially linear ethylene polymer for use in the  
30 invention are ethylene polymers having a PI in the range of 0.01 kpoise to 50 kpoise, preferably about 15 kpoise or less. The substantially linear ethylene polymers used herein can also be characterized as having a PI less than or equal to about 70 percent of the PI of a linear ethylene interpolymer  
35 (either a conventional Ziegler polymerized interpolymer or a linear homogeneously branched interpolymer as described by

Elston in US Patent 3,645,992) having an  $I_2$  and  $M_w/M_n$  and density, each within ten percent of the substantially linear ethylene interpolymer.

An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena and quantify the critical shear rate and critical shear stress of ethylene polymers. According to Ramamurthy in the Journal of Rheology, 30(2), pp. 337-357 (1986), the disclosure of which is incorporated herein by reference, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular film gloss to the more severe form of "sharkskin." Herein, as determined using the above-described GER, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40x magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers is at least about 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene interpolymer having essentially the same  $I_2$  and  $M_w/M_n$ .

Gross melt fracture occurs at unsteady extrusion flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability and optimum sealant properties, surface defects should be minimal, if not absent. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene interpolymers used in the invention, that is those having a density less than 0.91 g/cc, is greater than  $4 \times 10^6$  dynes/cm<sup>2</sup> (4000 MPa). The critical shear rate at the onset of surface melt fracture (OSMF) and the onset of gross melt fracture (OGMF) will be

used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. Preferably, in the present invention, the substantially linear ethylene polymer will be characterized by its critical shear rate, rather than its critical shear stress.

Preferred homogeneously branched ethylene interpolymers (for example substantially linear ethylene interpolymers) are characterized as having a single melting peak as determined using differential scanning calorimetry (DSC). However, for homogeneously branched ethylene interpolymers having a density of 0.875 g/cc to 0.91 g/cc, the single melt peak may show, depending on equipment sensitivity, a "shoulder" or a "hump" on the side low of the melting peak (that is below the melting point) that constitutes less than 12 percent, typically, less than 9 percent, more typically less than 6 percent of the total heat of fusion of the polymer. This artifact is due to intra-polymer chain variations, and it is discerned on the basis of the slope of the single melting peak varying monotonically through the melting region of the artifact. The artifact occurs within 34°C, typically within 27°C, and more typically within 20°C of the melting point of the single melting peak.

The single melting peak is determined using a differential scanning calorimeter standardized with indium and deionized water. The method involves 5-7 mg sample sizes, a "first heat" to 150°C which is held for 4 minutes, a cool down at 10°C/min. to -30°C which is held for 3 minutes, and heat up at 10°C/min. to 150°C to provide a "second heat" heat flow vs. temperature curve. Total heat of fusion of the polymer is calculated from the area under the curve. The heat of fusion attributable to a shoulder or hump artifact, if present, can be determined using an analytical balance and weight-percent calculations.

The molecular weight distributions of ethylene

polymers are determined by gel permeation chromatography (GPC) on a Waters 150C high temperature chromatographic unit equipped with a differential refractometer and three columns of mixed porosity. The columns are supplied by Polymer

Laboratories and are commonly packed with pore sizes of  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6 \text{\AA}$ . The solvent is 1,2,4-trichlorobenzene, from which about 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is about 1.0 milliliters/minute, unit operating temperature is about  $140^\circ\text{C}$  and the injection size is about 100 microliters.

The molecular weight determination with respect to the polymer backbone is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, p. 621, 1968, the disclosure of which is incorporated herein by reference) to derive the following equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b.$$

In this equation,  $a = 0.4316$  and  $b = 1.0$ . Weight average molecular weight,  $M_w$ , is calculated in the usual manner according to the following formula:  $M_j = (\sum w_i (M_i^j))^j$ ;

where  $w_i$  is the weight fraction of the molecules with molecular weight  $M_i$  eluting from the GPC column in fraction  $i$  and  $j = 1$  when calculating  $M_w$  and  $j = -1$  when calculating  $M_n$ .

For the at least one homogeneously branched ethylene polymer used in the present invention, the  $M_w/M_n$  is preferably less than 3.5, more preferably less than 3.0, most preferably less than 2.5, and especially in the range of from 1.5 to 2.5 and most especially in the range from 1.8 to 2.3.

Substantially linear ethylene polymers are known to have excellent processability, despite having a relatively

narrow molecular weight distribution (that is, the  $M_w/M_n$  ratio is typically less than about 3.5). Surprisingly, unlike homogeneously and heterogeneously branched linear ethylene polymers, the melt flow ratio ( $I_{10}/I_2$ ) of

5 substantially linear ethylene polymers can be varied essentially independently of the molecular weight distribution,  $M_w/M_n$ . Accordingly, especially when good extrusion processability is desired, the preferred ethylene polymer for use in the present invention is a homogeneously  
10 branched substantially linear ethylene interpolymer.

The density of the homogeneously branched ethylene polymer is preferably less than 0.93 grams/centimeter (g/cc), more preferably in the range from 0.85 g/cc to 0.92 g/cc, and most preferably in the range from 0.87 g/cc to 0.9 g/cc, as  
15 measured in accordance with ASTM D-792.

The molecular weight of the least one ethylene polymer can be conveniently determined using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition E" and also known as  $I_2$ ). Melt  
20 index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear.

Also, practitioners will recognized that the melt  
25 index of the at least one homogeneously branched ethylene polymer as well as the inventive composition itself can affect the heat seal strength of the resultant sealant film layer. That is, in generally and although the relationship is not necessarily linear, a lower melt index (that is,  
30 higher molecular weight) can yield a higher defined heat seal strength.

Preferably, the  $I_2$  melt index of the at least one ethylene polymer is in the range of from 0.01 to 50 g/10 minutes, more preferably from 0.1 to 20, and most preferably  
35 from 0.4 and 12 g/10 minutes.

Other measurements useful in characterizing the

molecular weight of ethylene polymer compositions involve melt index determinations with higher weights, such as, for common example, ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition N" and also known as  $I_{10}$ ). The ratio of a higher weight melt index determination to a lower weight determination is known as a melt flow ratio, and for measured  $I_{10}$  and the  $I_2$  melt index values the melt flow ratio is conveniently designated as  $I_{10}/I_2$ . Preferably, the at least ethylene polymer has an  $I_{10}/I_2$  melt flow ratio greater than or equal to 6.8, more preferably greater than or equal to 8 and most preferably in the range of from 8.5 to 20 and especially in the range of 9 to 15.

The at least one polybutylene polymer for use in the present invention preferably has a wide-angle X-ray diffraction crystallinity of less than 36 weight percent, based on the total weight of the polymer, more preferably less than or equal to 35 weight percent, based on the total weight of the polymer, most preferably less than 34 weight percent, based on the total weight of the polymer, or preferably in the range from 0 to 36 weight percent, based on the total weight of the polymer, more preferably in the range from 0 to 35 weight percent, based on the total weight of the polymer, most preferably in the range from 2 to 34 weight percent, based on the total weight of the polymer and most especially in the range from 8 to 32 weight percent, based on the total weight of the polymer.

The at least one polybutylene polymer can be an interpolymer for example, a copolymer of 1-butene polymerized with one other monomer such as, for example, but not limited to, another  $C_3$ - $C_{20}$   $\alpha$ -olefin, or a terpolymer of 1-butene interpolymerized with at least two other monomers wherein at least one of the at least two other monomers is a  $C_3$ - $C_{20}$   $\alpha$ -olefin. Examples of polybutylene interpolymers can include, but are not limited to, poly(1-butene/hexene) copolymers, poly(1-butene/pentene) copolymers, poly(1-butene/ethylene)

copolymers, poly(1-butene/propylene) copolymers, poly(1-butene/ethylene/propylene) terpolymers, .

Preferred polybutylene polymers for use in the present invention are poly(1-butene/ethylene) interpolymer, especially poly(1-butene/ethylene) copolymers. Preferred poly(1-butene/ethylene) interpolymers have an ethylene content greater than 5.4 weight percent, based on the total weight of the copolymer, preferably greater than or equal to 5.6 weight percent, based on the total weight of the copolymer, more preferably greater than 6 weight percent, based on the total weight of the polymer, or preferably in the range from 5.6 to 15.8 weight percent, based on the total weight of the copolymer, more preferably in the range from 6 to 15 weight percent, based on the total weight of the copolymer and most preferably in the range from 6.5 to 13.5 weight percent, based on the total weight of the copolymer. The ethylene content can be conveniently determined using known infra-red analysis techniques and the interrelationship between density, crystallinity and ethylene content for polybutylene polymers is shown in FIG. 11.

Suitable polybutylene polymers can be especially characterized by their polymer density wherein preferred polybutylene polymers for use in the present invention have densities of less than 0.897 g/cc, preferably less than or equal to 0.896 g/cc, more preferably less than 0.895, or preferably in the range of from 0.862 to 0.896, more preferably in the range of from 0.865 to 0.895 g/cc, and most preferably in the range of from 0.87 to 0.893 g/cc.

In addition to having a crystallinity less than 36 weight percent, based on the total weight of the polymer, especially preferred polybutylene polymers for use in the present invention also have a Ring and Ball softening point greater than or equal to 108°C to avoid excessive tackiness. Suitable polybutylene polymers can have an I<sub>2</sub> melt index in the range of from 0.01 to 1000 gram/10 minute.

Representative polybutylene polymers for use in the invention



are commercially available from Shell Chemical Company under the designations of DP 8310, DP 8510 and DP8910PC.

Suitable slip additives for use in the present invention as the at least one slip additive include silicon and amide containing compounds. A suitable silicon containing slip additive is polydimethylsiloxane which is supplied by Dow Corning Corporation. Suitable amides correspond to the general structure  $R - CO - NH_2$  where R is a saturated or unsaturated alkyl group. Suitable slip additives also correspond to the general structure  $R - CO - NH - R'$  where R and R' are saturated or unsaturated alkyl groups which can be the same or different as well as to the general structure  $R - CO - NH - A - NH - CO - R$  where R is either a saturated alkyl group or unsaturated alkyl group and A is an alkylene group, respectively. Preferred slip additives have the general structure  $R - CO - NH - R'$  where R and R' are saturated or unsaturated alkyl groups which can be the same or different and more preferably, R and R' are different such that the additives have mixed saturation (that is, either R or R' but not both is a saturated alkyl group and the other is an unsaturated alkyl group) and most preferably, R is an unsaturated alkyl group. Representative slip additives include, but are not limited to, erucamide, oleamide, oleyl palmitamide, stearyl erucamide, erucyl erucamide, oleyl oleamide, erucyl stearamide, ethylene bis-stearamide, and ethylene bis-oleamide. Preferred slip additives are oleyl palmitamide, stearyl erucamide, erucyl erucamide, oleyl oleamide, and erucyl stearamide, and oleyl palmitamide is the most preferred slip additive for use in the invention. Suitable slip additives are supplied commercially, for example, by Croda Universal Ltd. under the tradename of Crodamide.

Suitable silica-containing or calcium-containing additives for use in the present invention as the at least one silica-containing or calcium-containing additive include, but are not limited to, silicon dioxide (diatomaceous earth),

fumed silica, calcium carbonate, talc, clay, mica . Also, the silica-containing or calcium-containing additive can be treated or untreated. Preferred silica-containing or calcium-containing additives are treated to reduce or minimize absorption of the slip additives. Suitable treated silica-containing or calcium-containing additives are commercially supplied by Specialty Minerals, Inc. under the designation of POLYBLOC. Also, preferably, the at least one silica-containing or calcium-containing additive have a relatively narrow particle size distribution such that adverse affects on film optical properties are minimized. The most preferred silica-containing or calcium-containing additives are silica-containing and silicon dioxide (diatomaceous earth) is especially preferred.

The inventive composition preferably also comprises at least one other ethylene polymer as an optional incompatibilizer or carrier resin for the at least one amide slip additive and/or the at least one silica-containing or calcium-containing additive. That is, the additives are incorporated at specified amounts by the use of an additive concentrate, although the inventive composition can be prepared by direct incorporation of either or both types of additives. Preferably, the optional at least one ethylene polymer incompatibilizer or carrier resin is characterized as having long chain branching. However, more preferably the optional at least one ethylene polymer incompatibilizer or carrier resin is characterized as having long chain branching and a percent crystallinity at least 35 percent greater (not a unit difference, but a percentage difference), especially at least 40 percent greater, more especially at least 45 percent greater than and most especially at least 50 percent greater than the percent crystallinity of the at least one ethylene polymer sealant base resin, as determined using differential scanning calorimetry (DSC). Typically, the concentration of the additive(s) in the at least one optional ethylene polymer carrier resin is in the range of from 1 to

50 weight percent, based on the total of the concentrate. Preferably, separate concentrates are used for slip additives and silica-containing or calcium-containing additives, although the additives can be combined in a single carrier resin to provide a single additive concentrate of for the at least one slip additive and the at least one silica-containing or calcium-containing additive.

Suitable ethylene polymers for use in the present invention as the optional incompatibilizer or carrier resin include, but are not limited to, non-polar ethylene polymers such as homopolymer and interpolymers of ethylene and include homogeneously branched substantially linear ethylene polymers, homogeneously branched linear ethylene polymers, free-radical initiated high pressure low density polyethylene (LDPE) and heterogeneously branched linear ethylene polymers (that is, ultra or very low density polyethylene (ULDPE or VLDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), and high density polyethylene (HDPE) such as those manufactured using a Ziegler-Natta catalyst system) as well as combinations, polymer blends or mixtures thereof.

Although the above non-polar ethylene polymers are preferred for use as the optional incompatibilizer or concentrate carrier resin, polar ethylene polymer can also be employed. Such suitable polar ethylene polymers include, but are not limited to, anhydride modified polyethylenes (for example, succinnic anhydride and maleic anhydride grafted LDPE, LLDPE and HDPE) as well as free-radical initiated high pressure polyethylenes such as, for example, ethylene/acrylic acid (EAA) interpolymers, ethylene/vinyl acetate (EVA) interpolymers and ethylene/methacrylate (EMA) interpolymers and combinations, polymer blends or mixtures thereof. The preferred ethylene polymer incompatibilizer or carrier resins (that is, characterized as having long chain branching) include homogeneously branched substantially linear ethylene polymers and free-radical initiated high pressure

polyethylenes. Most preferably, the optional at least one ethylene polymer incompatibilizer or carrier resin is a different ethylene polymer than the at least one sealant base resin. Most especially, the optional at least one carrier resin for the at least one amide slip additive is low density polyethylene (LDPE).

The weight percent of the at least one optional ethylene polymer incompatibilizer or carrier resin is in the range from 0 to 50, based on the total weight of the composition.

The compositions can be made via any known technique, including, but not limited, dry blending and extrusion melt mixing of component polymers and in situ polymerizations and interpolymerizations that involve multiple reactors and/or multiple catalyst systems. Practitioners will recognize that melt mixing and high shear extrusion during fabrication can improve the homogeneity of compositions prepared by dry blending. Relative to the sealant base resin, such improvements can permit the use of lower quantities of polybutylene polymer and/or incompatibilizer.

The inventive sealant layer and film structure can be made using conventional fabrication techniques known in the art. Another embodiments of the invention include fabricating the inventive composition into the form of a sheet (that is, a film having a thickness greater than 20 mils), coating, and a thermoformed or molded article. As such, fabrication can include a lamination and coextrusion technique or combinations thereof, or using the inventive composition alone to provide a monolayer sealant film, and can also specifically include blown film, cast film, extrusion coating, injection molding, blow molding, thermoforming, profile extrusion, pultrusion, compression molding, rotomolding, or injection blow molding operations or combinations thereof. Fabrication multilayer film structures of the invention can also include elaborate orientation

techniques such as "tenter framing" or a "double bubble," "tape bubble," "trapped bubble" process or combinations thereof .

Packaging Foods With Plastics, by Wilmer A. Jenkins and James P. Harrington (1991); "Coextrusion For Barrier Packaging" by W.J. Schrenk and C.R. Finch, Society of Plastics Engineers RETEC Proceedings, June 15-17 (1981), pp. 211-229; K.R. Osborn and W.A. Jenkins in "Plastic Films, Technology and Packaging Applications" (Technomic Publishing Co., Inc. (1992)); and "Laminations Vs. Coextrusion" by D. Dumbleton (Converting Magazine (September 1992), the disclosures of all of which are incorporated herein by reference, describe blown or cast fabrication including lamination and coextrusion techniques. The double bubble technique is described by Pahkle in US Patent 3,456,044, the disclosure of which is incorporated herein by reference.

The composition or sealant layer of the invention has utility in a variety of peelable seal sealant applications. Suitable applications include, for example, but are not limited to, monolayer packaging films; multilayer packaging structures consisting of other materials such as, for example, high density polyethylene, biaxially oriented polypropylene or biaxially oriented ethylene polymer for shrink film and barrier shrink applications; packages formed via form/fill/seal machinery; packaging structures; cook-in food packages; compression filled packages; heat sealable stretch wrap packaging film such as, for example, fresh produce packaging and fresh red meat retail packaging; as well as in packages, containers, bags and lidding stock for uses such as, for example, but not limited, cereal box liners, cake mix packages, cracker tubes, medical device and item packaging, snack food convenience packages and containers, and gaskets.

Multilayer structures that include the inventive peelable seal sealant layer or composition may also include adhesion promoting tie layers (such as PRIMACOR™ ethylene-

acrylic acid (EAA) copolymers available from The Dow Chemical Company, and/or ethylene-vinyl acetate (EVA) copolymers. Such multilayer structures may further include additional structural layers such as AFFINITY™ polyolefin plastomers, available from The Dow Chemical Company, ENGAGE™ polyolefin elastomers, available from Dupont Dow Elastomers, DOWLEX™ LLDPE, available from The Dow Chemical Company, ATTANE™ ULDPE, available from The Dow Chemical Company, EXACT and EXCEED resins from The Exxon Chemical Corporation, TAFMER resins from Mitsui Chemical Corporation or blends of any of these polymers with each other or with another polymer, such as an EVA copolymer, a low density polyethylene (LDPE) resin or a high density polyethylene resin.

In general, multilayer structures that include the peelable seal sealant layer or composition of the present invention (whether biaxially or monoaxially oriented or not) can include, but are not limited to, barrier layers, tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more than one layer in the same multilayer structure. Some of these materials include: paper, glassine, foil, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), polypropylene (especially, oriented polypropylene (OPP) and more especially, biaxially oriented polypropylene), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, ULDPE, LLDPE, HDPE, MDPE, LMDPE, LDPE, ionomers, and graft-modified polymers (for example, maleic anhydride grafted polyethylene).

Generally, the film structure of the present invention can comprise any number of layers or materials or polymers deemed required for a targeted application, including more than one inventive sealant layer as well as only one layer (monolayer film). However, typically, film structure of the invention comprises from 2 to 7 layers.

Practitioners will recognize that higher sealant layer thicknesses will generally tend to increase seal strength. In general, sealant layer and film structure can be of any thickness demanded by a particular target application. The thickness of film or multilayer structures made from or with the inventive composition or sealant layer can range from 0.3 to 20 mils, preferably from 0.4 to 12 mils. For packaging or containing high-sugar content food and moisture or flavor sensitive items, structure thicknesses will generally be higher. The inventive sealant layer itself can be of any thickness. However, generally, the sealant layer has a thickness in the range of 0.1 to 1 mil (0.0025 to 0.025 mm).

#### EXAMPLES

In an evaluation to provide a peelable seal composition with improved seal performance several ethylene polymer compositions were studied. The compositions differed according to weight percentage polybutylene polymer dry tumble blended with a substantially linear ethylene polymer.

The substantially linear ethylene polymer, supplied by The Dow Chemical Company, had an I<sub>2</sub> melt index of 1.6 g/10 minutes, a density of 0.895 g/cc and a DSC crystallinity of about 29 weight percent. The polybutylene polymer, supplied by Shell Chemical Company, was a poly(1-butene/ethylene) copolymer having an I<sub>2</sub> melt index of 3.0, a density of 0.8965 g/cc, an ethylene content of 6 weight percent and a wide-angle X-ray diffraction crystallinity of 34 weight percent.

All Examples contained 10 weight percent Ampacet 10516 slip and antiblock concentrate which comprised 4 weight percent erucamide, 4 weight percent oleamide, 20 weight percent diatomaceous earth silicon dioxide (each based on the total weight of the concentrate) and a free-radical initiated, high pressure low density polyethylene (LDPE) resin as the carrier resin. The LDPE carrier resin had an I<sub>2</sub> melt index of 8 g/10

minutes, a density of 0.918 g/cc, a DSC crystallinity of about 44.9 weight percent (based on the total weight of the polymer) and constituted 7.2 weight percent of each Example (based on the total weight of the composition).

FIG. 21 shows the interrelationship between DSC crystallinity and polymer density for non-polar ethylene polymers. Table 1 shows the description of the various sealant layer Examples (that is, Inventive Examples 1, 2 and 8 and comparative examples 3-7).

**Table 1**

Example	Weight Percent SLEP*	Weight Percent PB**
Inventive Ex. 1	55	35
Inventive Ex. 2	50	40
Comparative Ex. 3	90	0
Comparative Ex. 4	80	10
Comparative Ex. 5	75	15
Comparative Ex. 6	70	20
Comparative Ex. 7	65	25
Inventive Ex. 8	60	30

\*SLEP denotes a substantially linear ethylene polymer as the base sealant resin.

\*\*PB denotes poly(1-butene/ethylene) copolymer as the blend component of the base sealant resin.

The film structures used in this evaluation were three-layer coextruded blown films comprised of the following layers (going from the outside skin layer to the peelable seal sealant layer) HDPE/HDPE/peelable seal sealant layer. The coextrusion fabrication unit consisted of three extruders in an ABC configuration. Extruder A was a 2.5 inch (6.4 cm) diameter, 24:1 L/D extruder which was used to extrude outside peelable seal layer. Extruder B was a 2.5 inch (6.4 cm), 24:1 L/D extruder which was used to extrude the HDPE core layer. Extruder C was a 2 inch (5.1 cm), 24:1 L/D extruder which was used to extrude the HDPE the outside skin layer. Total film thickness was targeted at 2.2 mils (0.056 mm) and the peelable sealant layer constituted 13 weight percent of the film structure (that is, 0.28-0.3 mil (0.0071-0.0076 mm)). The HDPE resin used for the core layer and outside skin layer was Chevron HDPE 9650 which had an I<sub>2</sub> melt index



of 0.3 g/10 minutes and a density of 0.952 g/cc. The targeted melt temperature for the coextrusion ranged from 400-450°F (204-232°) and the die gap was set at 70 mils (1.8 mm).

5 After fabrication the various film structures (Examples) were permitted to age 8 days, 22 days and 37 days before being tested for sealing performance properties. To determine the sealing performance properties of the Examples, one inch (25 mm) wide strips were mounted on a Topwave Hot  
10 Tack Tester, Model DTC 52D. Sealing conditions consisted of a 0.5 second dwell time and a 40 psi (0.275 MPa) seal bar pressure. After being formed, seals were stored at ASTM conditions (22°C, 50percent RH) for about 48 hours and then  
15 pulled on an Instron tensiometer at a crosshead speed of 10 in/min (250 mm/min). Heat seal strengths are reported in pounds/inch (lbs./inch).

For this study, heat seal initiation performance was defined as the heat seal strength of obtained for the Example at 90°C and 100°C as well as the temperature at which  
20 a heat seal strength of at least about 1.5 lbs./inch (0.27 kg/cm) width was obtained. A defined or targeted heat seal strength was set at the range of 1.8 to 3.2 lbs./inch (0.32 to 0.57 kg/cm) and as such the sealing window was taken as that range of sealing temperature wherein the heat seal  
25 strength of the Example was within the range of 1.8 to 3.2 lbs./inch. Tables 2-4 shows the raw initial and aged heat seal data.

Table 5 shows the aged heat seal initiation performance data and sealing window/plateau data for the  
30 respective Examples. Table 6 shows the median heat seal strengths and the percent average deviations for the Examples. FIG. 2, 3 and 4 show the heat sealing profiles for the initial 8 day, 22 day and 37 day film samples, respectively.

35 These figures and Table 5 indicate that Inventive Examples 1, 2 and 8 exhibit excellent peelable seal sealing

performance. With respect to heat initiation performance, at a sealing temperature of less than or equal to 100°C, heat seal strengths for the inventive examples were easily in the range of 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm). The  
5 inventive examples also had broad sealing windows at a defined heat seal strength of 1.8 to 3.2 lbs./inch (0.32 to 0.57 kg/cm). Table 5 shows that Inventive Examples 1, 2 and 8 all maintained sealing window plateaus of at least 20°C for the defined heat seal strength of 1.8 to 3.2 lbs./inch (0.32  
10 to 0.57 kg/cm) for at least 22 days following initial film fabrication, and for at least 37 days for Inventive Examples 1 and 2.

Table 6 indicates that Inventive Examples 1, 2 and 8 have percent average deviations of less than or equal to  
15 16.5 percent in the range of 90°-140°C and 100°-130°C for up to 37 days after initial film fabrication. This relatively low average deviation is indicative of excellent sealing consistency and stability. This result is surprisingly as it is contrary to the disclosure discussed herein above which  
20 indicated that polybutylene polymers are subject to "aging down" and that blending levels of polybutylene polymers should be maintained at relatively low or minor levels to avoid sealing inconsistencies.

Interestingly, comparative example 7 which was also  
25 prepared at relatively high levels of polybutylene polymer (that is, 25 weight percent) initially exhibited a relatively broad sealing window plateaus; however, as shown in Table 5, comparative example 7 followed the expected behavior of substantially "aging down" after 22 days of aging following  
30 film fabrication and Table 6 shows that comparative example 7 had a relatively high percent average deviation for the temperature ranges of 100°-130°C and 90°-140°C (that is, from 17.7 to 34.3percent).

The other comparative examples in the evaluation  
35 (that is, comparative examples 3-6) did not provide or

develop a substantial sealing window plateau during the evaluation period. Comparative examples 3, 4, 5 and 6 all exhibited very narrow sealing windows with sealing window plateaus of less than 8°C for a defined heat seal strength of 1.8 to 3.2 lbs./inch (0.32 to 0.57 kg/cm). Also, comparative examples 3, 4, 5, 6 and 7, for the initial 8 day sealing data, all had a heat seal initiation performances which reflected their less than desirable sealing profiles. Specifically, as shown in Table 4, comparative examples 3, 4, 5 and 6 all had heat seal strengths greater than 3.5 lbs./inch (0.64 kg/cm) at 100°C.

FIG. 5 and 6 which are plots heat seal strength at 90°C and 100°C, respectively, versus weight percent polybutylene polymer (Shell DP8310) for Inventive Examples 1, 2 and 8 and comparative 3-7 aged 8 days, 22 days and 37 days shows only Inventive Examples 1, 2 and 8 provide a heat seal initiation performance wherein a heat seal strength in the range of 1.6 to 3.2 lbs./inch (0.28 to 0.57 kg/cm) is obtained after aging for less than or equal to 8 days following film fabrication. These figures also show that Inventive Examples 1, 2 and 8 all provide a heat seal strength within the defined range of 1.8 to 3.2 lbs./inch (0.32 to 0.57 kg/cm) for up to 37 days of aging following initial film fabrication. The excellent, consistent and stable sealing performance observed for inventive examples is simply not matched by the comparative examples. Further, these figures surprisingly show that after decreasing seal strengths at 90°C and 100°C at lower levels, higher levels of the polybutylene polymer (as specified by the present invention) blended with a homogeneously branched substantially linear ethylene worked to provide excellent seal initiation performance. This discontinuity in seal initiation performance as a function of weight percent polybutylene polymer was completely unexpected as higher levels are expected yield poor sealing characteristics.

The hot tack performance of the various Examples was determined for the initial 8 day, 27 day and 37 day aging times. Hot tack testing followed heat seal testing described above except seals were pulled after a 0.2 second delay  
5 (instead of after about 48 hours of conditioning) at a rate of 150 mm/second. Tables 7, 8 and 9 provide the raw hot tack data (in Newtons/inch) and FIG. 7-9 show the hot tack profiles for the various Examples.

**Table 2**  
Heat Seal Strength (in lbs./inch) 8 Days After Film Fabrication

Sealing Temperature °C	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
70			0.03					
75	0.62		1.27	0.04	0.28			
80	0.8	0.68	2.94	0.55	1.04	0.78		
85	1.49	1.6	4.18	2.03	2.71	3.47	0.22	1.05
90	2.4	2.22	5.74	3.29	3.53	3.77	0.95	2.36
95	3.11	2.73	6.38	4.27	4.81	4.15	1.87	2.9
100	2.85	2.95	7.69	4.59	5.7	4.77	1.93	2.9
105	2.95	3.16	7.69	6.16	6.11	3.75	2.01	2.8
110	2.55	3.03	8.34	6.38	6.4	4.61	2.28	3.1
115	2.58	2.97	8.58	6.21	6.6	4.93	2.59	3.26
120	2.65	2.72	8.39	7.26	6.33	4.28	2.93	3.52
125	3.07	3.03	9.15	7.65	6.7	5.18	3.03	3.33
130	3.51	3.17		8.37	8.07	4.87	4.08	3.82
140	3.48	3.43		8.44	8.19	7.78	4.52	4.23
150	4.02	5.71		7.68	7.75	7.41	5.21	4.25

**Table 3**  
Heat Seal Strength (in lbs./inch) 22 Days After Film Fabrication

Sealing Temperature °C	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
75	0.69	0.81	0.41					
80	0.94	0.83	1.5	0.13	0.21	0.39		0.73
85	2.03	1.58	3.86	0.89	2.17	2.20	0.45	1.75
90	2.44	1.97	3.42	2.81	3.3	2.59	1.10	2.33
95	2.61	2.53	6.48	4.65	4.25	4.36	1.52	2.54
100	2.77	3.02	6.86	4.95	5.74	4.00	1.68	2.78
105	2.68	2.86	8.43	4.83	6.68	3.18	2.11	3.01
110	2.55	2.98	8.24	6.59	6.58	3.41	2.71	3.27
115	2.81	2.81	7.92	6.15	7.54	4.34	2.87	3.38
120	2.60	3.0	8.83	6.8	6.84	3.95	3.53	3.44
125	2.57	2.94		6.7	6.54	4.03	3.16	3.39
130	3.16	3.07		7.94	7.68	6.66	4.79	3.80
140	3.54	3.75		8.24	8.87	6.23	4.33	4.28

**Table 4**  
Heat Seal Strength (in lbs./inch) 37 Days After Film Fabrication

Sealing Temperature °C	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
75	0.66	0.84	0.50					
80	0.93	1.30	1.74	0.33	0.26	0.48	0.18	0.70
85	2.04	1.81	4.09	1.68	2.59	2.30	0.66	2.37
90	2.24	2.66	6.71	2.97	4.11	2.00	1.56	2.81
95	2.83	3.08	7.55	3.68	3.57	4.76	1.96	3.55
100	3.20	3.15	7.72	4.33	4.30	4.37	2.37	3.33
105	2.83	2.93	7.75	5.63	6.03	4.13	2.57	3.38
110	2.92	3.00	8.27	6.31	5.68	4.17	3.17	3.11
115	3.04	3.08	9.17	6.36	6.23	4.37	3.40	3.44
120	3.01	3.00	8.01	6.85	6.20	4.62	3.59	3.97
125	3.08	3.05		7.19	7.29	4.62	3.79	3.94
130	4.06	3.35		8.67	8.52	6.23	4.94	4.81
140	4.16	4.50		8.38	8.65	6.37	5.14	5.06

**Table 5**  
Effect of Aging on Heat Seal Initiation Temperature and Sealing Window\*

Example	Initial (8 Day) Seal Initiation Temperature @ 1.5 lbs./inch, °C	22 Day Seal Initiation Temperature @ 1.5 lbs./inch, °C	37 Day Seal Initiation Temperature @ 1.5 lbs./inch, °C	Initial (8 Day) Sealing Window @ 1.8-3.2 Lbs./inch, °C	22 Day Sealing Window, °C @ 1.8-3.2 Lbs./inch	37 Day Sealing Window, °C @ 1.8-3.2 Lbs./inch
Inv. Ex 1	85	82.5	82.5	39.5	46	41.5
Inv. Ex 2	85	84	82.5	48	43	42.5
Comp. Ex 3	76	80	78	4.5	3	2.5
Comp. Ex 4	83	86.5	84.5	5.5	3.5	6
Comp. Ex 5	81	83	82.5	6	5.5	3
Comp. Ex 6	81	83	83.5	4	7.5	8
Comp. Ex 7	93	95	90	31.5	15	18
Inv. Ex 8	86.5	84	82.5	25.5	23	9

\*All values in this table are approximations taken visually from corresponding figures.

**Table 6**  
Heat Seal Strength Medians and Percent Average Deviations

	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
<b>8 Days</b>								
Median <sub>90-140°C</sub>	2.9	3.00	8.02*	6.30	6.37	4.69	2.44	3.18
Average								
Deviation <sub>90-140°C</sub>	0.309	0.231	0.870*	1.358	0.965	0.705	0.817	0.410
Percent Average								
Deviation	10.7%	7.7%	10.9%	21.6%	15.2%	15.0%	33.5%	12.9%
<b>22 Days</b>								
Median <sub>90-140°C</sub>	2.65	2.96	7.92*	6.37	6.63	4.02	2.79	3.33
Average								
Deviation <sub>90-140°C</sub>	0.238	0.280	1.356*	1.325	1.183	0.898	0.956	0.446
% Average								
Deviation	9.0%	9.5%	17.1%	20.8%	17.8%	22.4%	34.3%	13.4%
<b>37 Days</b>								
Median <sub>90-140°C</sub>	3.03	3.07	7.75*	6.34	6.12	4.50	3.29	3.50
Average								
Deviation <sub>90-140°C</sub>	0.402	0.298	0.515*	1.508	1.320	0.756	0.923	0.564
% Average								
Deviation	13.3%	9.7%	6.6%	23.8%	21.6%	16.8%	28.1%	16.1%
<b>8 Days</b>								
Median <sub>100-130°C</sub>	2.85	3.03	8.365*	6.38	6.4	4.77	2.59	3.26
Average								
Deviation <sub>100-130°C</sub>	0.254	0.107	0.411*	0.943	0.484	0.355	0.560	0.269
% Average								
Deviation	8.9%	3.5%	4.9%	14.8%	7.6%	7.4%	21.6%	8.3%
<b>22 Days</b>								
Median <sub>100-130°C</sub>	2.68	2.98	8.24*	6.59	6.68	4.00	2.87	3.38
Average								
Deviation <sub>100-130°C</sub>	0.153	0.072	0.533*	0.831	0.474	0.729	0.727	0.236
% Average								
Deviation	5.7%	2.4%	6.5%	12.6%	7.1%	18.2%	25.3%	7.0%
<b>37 Days</b>								
Median <sub>100-130°C</sub>	3.04	3.05	8.01*	6.36	6.2	4.37	3.4	3.44
Average								
Deviation <sub>100-130°C</sub>	0.267	0.097	0.429*	0.937	0.905	0.453	0.602	0.453
% Average								
Deviation	8.8%	3.2%	5.4%	14.7%	14.6%	10.4%	17.7%	13.2%

\*Denotes the average deviation was computed for temperature points of 90°, 95°, 100°, 105°, 110°, 115°, 120° and 125°C for the temperature range of 90-140°C (that is, n = 8).

\*Denotes the average deviation was computed for temperature points of 90°, 95°, 100°, 105°, 110°, 115° and 120°C for the temperature range of 90-140°C (that is, n = 7) and 100°, 105°, 110°, 115° and 120°C for the temperature range of 90-140°C (n = 5).

**Table 7**  
Hot Tack Strength (Newtons/inch) 8 Days After Film Fabrication

Sealing Temperature, °C	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
60	0.6	0.5		0.2			0.7	0.3
65	2.6	3.1		1.4	0.8	0.4	2.3	3.8
70	5.7	8.5	0.8	2.1	2.4	3.5	5.4	4
75	6.8	7.9		3	2.5	3.6	5	4.4
80	6.5	7.8	2.2	3.8	3.1	4.3	5.3	5.1
85	7	8.3	3.6	4.4	4.2	4.9	5.4	6.1
90	7.2	8.4	4.6	4.3	4.1	4.4	5	4.8
95	8	7.5	4	4.2	3.9	3.8	5.3	5.4
100	7.3	8	3.1	3.5	3.6	4	5.2	5.2
105	7.2	8	2.7	3.6	3.3	3.8	3.5	3.9
110	6.9	7.7	2.4	3.9	3.4	4.4	3.8	4.2
115	6.5	6.9	2.4	3.3	2.7	3.8	3.7	4.5
120	5.8	6.3	1.8	2.9	2.7	3.3	3.4	3.8
125	4	5.3	2.1	1.6	2.6	3.3	3.3	3.1
130	2.6	3.9	1.5	1.1	1.9	2.3	2.5	2.6
140	2.6	2.1	1.1	0.9	1.5	1.7	1.5	1.7
150	0.7	2	1		0.8	1.3	1.3	1.4



**Table 8**  
Hot Tack Strength (Newtons/inch) 22 Days After Film Fabrication

Sealing Temperature, °C	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
60	0.80	0.70				0.20	1.10	0.30
65	2.90	4.70				1.90	4.70	1.90
70	4.20	5.50		0.70	0.90	1.90	5.60	3.60
75	4.50	7.50	0.20	2.10	2.30	3.60	5.90	5.20
80	5.70	7.20	2.50	3.60	3.30	4.40	5.60	5.00
85	7.00	7.60	4.10	4.60	4.00	5.20	5.70	4.60
90	5.20	6.00	3.50	4.50	5.00	5.00	5.00	5.30
95	4.70	6.20	5.20	4.50	4.80	4.60	5.40	3.40
100	4.50	6.30	4.10	4.20	4.20	4.50	4.20	3.70
105	5.00	5.50	3.80	3.60	3.90	3.90	4.20	3.70
110	4.60	5.60	2.50	3.50	3.30	3.90	4.50	4.10
115	5.10	5.70	2.30	2.60	3.20	3.90	4.30	4.70
120	4.20	5.00	1.90	2.90	2.60	3.30	4.00	4.30
125	4.40	4.60	1.90	2.90	2.50	2.50	3.30	3.70
130	3.80	3.90	1.70	1.50	1.70	2.20	2.20	2.70
140	2.00	2.00	1.40	1.10	1.30	1.70	1.90	2.00
150			0.90					

**Table 9**  
Hot Tack Strength (Newtons/inch) 37 Days After Film Fabrication

Sealing Temperature °C	Inv. Ex 1	Inv. Ex 2	Comp. Ex 3	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp. Ex 7	Inv. Ex 8
55								
60	0.88	0.62		0.20			0.66	0.25
65	4.35	3.42	0.24	1.32	0.74	0.70	4.58	4.94
70	5.42	7.45	1.18	2.49	1.70	2.70	5.17	5.30
75	5.46	6.94	1.66	3.37	2.74	3.80	5.68	5.50
80	5.49	7.23	2.55	3.59	3.23	4.10	5.08	5.10
85	6.60	7.00	4.23	4.29	4.65	4.80	5.45	5.41
90	6.03	5.72	4.65	4.18	4.47	4.10	5.64	5.48
95	5.45	7.09	3.92	3.72	3.61	4.20	5.32	4.88
100	6.84	6.89	3.10	3.11	3.34	4.10	5.53	5.84
105	6.36	5.55	2.69	3.37	3.28	3.90	5.11	5.09
110	4.49	6.16	2.34	3.04	3.31	3.90	5.62	4.62
115	4.77	5.75	2.34	3.10	3.08	3.80	4.74	4.51
120	5.51	5.51	1.75	3.51	3.17	3.30	4.56	3.56
125	4.07	4.62	1.77	2.78	2.83	3.30	3.76	3.49
130	2.90	3.70	1.46	1.86	2.03	2.50	4.42	2.16
140	2.41	3.59	1.32	1.37	1.39	1.70	2.23	

FIG. 7-9 indicate that hot tack strength also surprisingly (in view of the compatibility concerns described above) improved at high levels of the polybutylene polymer. These figures also show that (identical to heat seal performance shown in FIG. 5 and 6) that the higher levels of polybutylene polymer specified by the present invention provided desirably low hot tack initiation temperatures and broadened hot tack windows at high hot tack strengths. Also, for Inventive Examples 1, 2 and 8, hot tack performance desirably paralleled their respective heat seal performances.

Comparative examples 9, 10, 11 and 12

In another evaluation, the performance attributes of four different polybutylene polymers were compared. The first polybutylene polymer was the same as employed for Inventive Examples 1, 2 and 8 above (that is, Duraflex DP 8310 supplied by Shell Chemical Corporation).

The second polybutylene polymer was Duraflex 8640 which was specifically recommended for use in peelable seal formulations by the manufacturer, Shell Chemical Corporation. According to product brochure information, the Duraflex 8640 product was a poly(1-butene/ethylene) copolymer having an I<sub>2</sub> melt index of 1.0 g/10 minutes, a density of 0.908 g/cc and a low ethylene content. From the reported density, this polymer was believed to contain about 2 weight percent ethylene, based on the total weight of the copolymer and have a wide angle X-ray diffraction crystallinity of about 48 weight percent, based on the total weight of the copolymer.

The third polybutylene polymer was a homopolymer supplied commercially by Shell Chemical Corporation under the designation of Duraflex 0110. This polybutylene polymer reportedly has a crystallinity of about 55 weight percent, an I<sub>2</sub> melt index of 0.4 g/10 minutes and a density of 0.915 g/cc.

The fourth polybutylene polymer was a poly(1-butene/ethylene) copolymer having a medium ethylene content. This polybutylene polymer was supplied by Shell Chemical

Corporation under the designation of WBS 425 with an I<sub>2</sub> melt index of 2.0 g/10 minutes and a density of 0.905 g/cc. From the reported density, FIG. 10 (which plots polybutylene polymer density and ethylene content versus weight percent crystallinity) indicated that this polymer contained about 3 weight percent ethylene, based on the total weight of the copolymer, and had a wide-angle X ray diffraction crystallinity of about 44 weight percent, based on the total weight of the copolymer.

In this evaluation, each polybutylene polymer was dry tumble blended (at 35 weight percent, based on the total weight of the final formulation) with the same substantially linear ethylene polymer as employed for Inventive Examples 1, 2 and 8. To each formulation, 2500 ppm of erucamide slip additive and 5000 ppm of diatomaceous earth silicon dioxide was directly incorporated.

The formulation comprising Duraflex DP 8310 was designated comparative example 9. The formulation comprising WBS 425 was designated comparative example 10. The formulation comprising Duraflex 8640 was designated comparative example 11. The formulation comprising Duraflex 0110 was designated comparative example 12.

Each formulation was utilized as a peelable seal sealant layer and fabricated into a three layer coextruded as described for Inventive Examples 1, 2 and 8 except the total film thickness was 2.0 mils (0.051 mm) with the sealant layer constituting 0.5 mils (0.013 mm), the HDPE core layer constituting 0.9 mils (0.023 mm) and the HDPE skin outside layer constituting 0.6 mils (0.015 mm).

Heat seal and hot tack performance was determined for each Example 7 days after film fabrication using the heat seal test conditions described above for Inventive Examples 1, 2 and 8 except seals heat were pulled after 24 hours of aging at ASTM conditions of 23°C and 50 percent relative humidity. Film clarity and haze properties were also determined for each Example in accordance with ASTM D-2457

and ASTM D1003, respectively. The sealant-to-sealant kinetic coefficient of friction was determined for each Example in accordance with ASTM D1894.

The puncture resistance of each Example was  
5 determined using an Instron tensiometer equipped with a strain cell and an integrated digital display that provides force determinations. A single ply of the blown coextruded films were mounted taut between the two halves of a circular holder constructed of aluminum and machined to couple the  
10 halves securely when joined together. The exposed film area when mounted in the holder was 4 inches (10.2 cm) in diameter. The holder was then affixed to the upper stationary jaw of the tensiometer. To the lower jaw of the tensiometer which was set to traverse upwardly, a  
15 hemispherical aluminum probe having a 12.5 mm diameter was affixed. The probe was aligned to traverse upwards through the center of the mounted film at a deformation rate of 250 mm/min. The force required to rupture the film was taken from the digital display and divided by the film thickness  
20 and the diameter of the probe to provide puncture resistance in kg-cm/cc.

Table 10 shows the raw heat seal strength data and the average deviations for comparative examples 9, 10 and 11. FIG. 11 shows the heat seal profiles of comparative examples  
25 9, 10, 11 and 12. FIG. 12 shows the hot tack profiles of comparative examples 9, 10 and 11. FIG. 13 shows the clarity comparison between comparative examples 9, 10 and 11. FIG. 14 shows the percent haze comparison between comparative examples 9, 10 and 11. FIG. 15 shows the puncture resistance  
30 comparison between comparative examples 9, 10 and 11. FIG. 16 and 17 show the film to metal and film to film COF comparisons, respectively, between comparative examples 9, 10 and 11.

5

**Table 10**  
**Heat Seal Strength (lbs./inch)**

Sealing Temperature, °C	Comp. Ex 9	Comp. Ex 10	Comp. Ex 11	Comp. Ex 12
65	0.59			
70	1.07			
75	1.18		0.16	
80	1.55		0.46	0.20
85	2.11	0.58	0.94	0.25
90	1.50	1.55	1.57	0.40
95	2.40	1.63	1.31	0.80
100	3.70	1.93	1.55	0.90
105	3.23	1.92	1.58	0.95
110	3.53	2.76	3.30	1.40
115	3.46	2.59	5.52	1.65
120	3.09	2.12	5.50	4.20
125	3.00	2.43	6.02	
130	2.61	2.88	6.57	5.40
140	2.83	3.03	6.29	
150	3.24	2.55	4.57	5.20
<b>Median<sub>90-140°C</sub></b>	<b>3.045</b>	<b>2.275</b>	<b>4.40</b>	<b>1.175*</b>
<b>Average Deviation<sub>90-140°C</sub></b>	<b>0.480</b>	<b>0.454</b>	<b>2.059</b>	<b>1.419*</b>
<b>% Average Deviation</b>	<b>15.8%</b>	<b>20.0%</b>	<b>46.8%</b>	<b>120.7%</b>
<b>Median<sub>100-130°C</sub></b>	<b>3.23</b>	<b>2.43</b>	<b>5.50</b>	<b>1.53</b>
<b>Average Deviation<sub>100-130°C</sub></b>	<b>0.284</b>	<b>0.331</b>	<b>1.841</b>	<b>1.589</b>
<b>% Average Deviation</b>	<b>8.8%</b>	<b>13.6%</b>	<b>33.5%</b>	<b>104.2%</b>

\*Denotes the average deviation was computed for temperature points of 90°, 95°, 100°, 105°, 110°, 115°, 120° and 125°C for the temperature range of 90-140°C (that is,  $n = 8$ ) and 100°, 105°, 110°, 115°, 120° and 125°C for the temperature range of 100-130°C (that is,  $n = 6$ ).

The data in Table 10 and FIG. 11-17 indicates that in direct comparisons, polybutylene polymers having higher ethylene contents provide peelable seal sealant layers with improved properties. Property improvements for sealant layers comprising a high ethylene content polybutylene polymer (that is, comparative example 9 in this evaluation) included a lower percent average deviation, a broader sealing window plateau for the temperature range of 70-150°C which consisted of a lower heat seal initiation temperature (that is, about 78.5°C for a heat seal strength of 1.5 lbs./inch (0.27 kg/cm)) as well as superior optical properties and

comparable COF performance. Also, desirably comparative example 9 (as well as comparative examples 11 and 12) exhibited cohesive seal failure, while comparative example 10 exhibited adhesive failure and as such did not have the desired tamper-evident, aesthetically attractive opened-seal characteristics.

However, although improved in important ways relative to comparative examples 10-12, comparative example 9 did not meet the objects of the invention. For example, comparative example 9 exhibits a double plateau for the defined heat seal strength of 1.8-3.2 lbs./inch (0.32-0.57 kg/cm) and with regard to heat seal initiation performance, Table 10 and FIG. 11 show comparative example 9 had a heat seal strength of 1.5 lbs./inch (0.27 kg/cm) at about 78.5°C and at 90°C and a heat seal strength greater than 3.5 lbs./inch (0.64 kg/cm) at 100°C (that is, measured 3.7 lbs./inch (0.66 kg/cm) at 100°C) which was indicative of an undesirably steep sealing profile at low sealing temperatures. The inferior performance of comparative example 9 relative to Inventive Examples 1, 2 and 8 was attributed to its relatively low slip additive level (that is, 2500 ppm erucamide).

In another evaluation, various formulations were prepared to determine the effects of different slip additives, different carrier resins, different silica-containing or calcium-containing additives as well as different polybutylene polymers. Table 11 provides the descriptions of the various Examples which were prepared by dry blending polymers and additive concentrates together in a tumble blender for 30 minutes. As indicated in Table 11, Inventive Examples 16 and 17 and Inventive Examples 19 and 20 had the same formulation. The difference between these two pairs was the later of each pair was aged for 15 days. Although not indicated in Table 11, the silica-containing or calcium-containing additives (that is, SiO<sub>2</sub> and talc) were

incorporated via concentrates comprised of the same LDPE carrier resin as indicated for Inventive Example 15.

Inventive Examples 14-17 and 19-20 comparative examples 18 and 21-23 were utilized as peelable seal sealant layers and fabricated into a three layer coextruded film having a total thickness of 2.2 mils wherein the sealant layer ratio was 13 percent as described for Inventive Examples 1, 2 and 8.

Table 12 provides the raw heat seal data and the percent average deviation computations for each Example. All Examples except Inventive Examples 17 and 20 were aged 7 days at 23°C and 50 percent relative humidity. Heat seal performance of the Examples was determined as described for Inventive Examples 1, 2 and 8 using one inch (25 mm) wide strips of the coextruded film mounted on a Topwave Hot Tack Tester, Model DTC 52D. Sealing conditions consisted of a 0.5 second dwell time and a 40 psi (0.275 MPa) seal bar pressure. FIG. 18 and 19 show heat seal profile comparisons for the Examples in this evaluation.

Hot tack performance for the Examples was also performed on a Topwave Hot Tack Tester set at a sealing dwell time of 0.5 second, a delay time of 0.1 second, a peel speed of 150 millimeter (mm)/second, and a sealing pressure of 40 psi (0.275 MPa). Table 13 provides the raw hot tack data for the Examples aged 7 days. Hot tack strength is reported in Newtons/inch width (Newtons/25.4 mm width).

Table 14 provides COF for data for the Examples aged up to 14 or 15 days after film fabrication and FIG. 20 plots the sealant-to-sealant kinetic COF for Inventive Examples 14, 15 and 16 and comparative example 18. Table 15 provides the abuse properties (that is, puncture and tear resistance) determined for Inventive Examples 14 and 15 and comparative example 18.

Sensory data (taste characteristics) on selected Examples were also generated using trained panelists and by employing a ranking format of paired comparisons and a



balanced block design in order to minimize bias. The transfer media for the sensory evaluation was ambient temperature spring drinking water.

**Table 11**  
Example Descriptions

Example	Sealant Base Resin	Polybutylene Polymer	Slip Additive Carrier Resin	Erucamide Level (ppm)	Oleamide Level (ppm)	Oleyl Palmitamide Level (ppm)	Polydimethylsiloxane (ppm)	SiO <sub>2</sub> Level (ppm)	Talc Level (ppm)
Inv. Ex 14	54% SLEP1	35% PB1	11% SLEP3	7500	0	0	0	0	6000
Inv. Ex 15	46.75% SLEP2	35% PB1	18.25% LDPE	7500	0	0	0	10000	0
Inv. Ex 16/17	40.5% SLEP2	35% PB1	22.525% LDPE	0	0	9750	0	10000	0
Comp. Ex 18	46.75% SLEP2	35% PB2	18.25% LDPE	7500	0	0	0	10000	0
Inv. Ex 19/20	56% SLEP2	35% PB1	7% LDPE	0	0	0	10000	10000	0
Comp. Ex 21	EVA	12% PB3	LDPE	800	800	0	0	4000	0
Comp. Ex 22	EVA	10% PB3	LDPE	1200	1200	0	0	6000	0
Comp. Ex 23	EVA	15% PB3	LDPE	1200	1200	0	0	6000	0

SLEP1 was a homogeneously branched substantially linear ethylene polymer having a 1.0 g/10 minute I<sub>2</sub> melt index, a 0.8965 g/cc density and DSC crystallinity of ~29.7 weight percent supplied by The Dow Chemical Company.

SLEP2 was a homogeneously branched substantially linear ethylene polymer having a 1.6 g/10 minute I<sub>2</sub> melt index, a 0.8965 g/cc density and DSC crystallinity of ~29.7 weight percent supplied by The Dow Chemical Company.

SLEP3 was a homogeneously branched substantially linear ethylene polymer having a 6 g/10 minute I<sub>2</sub> melt index, a 0.911 g/cc density and DSC crystallinity of ~40.1 weight percent supplied by The Dow Chemical Company.

PB1 was a poly(1-butene/ethylene) copolymer containing 6 weight percent ethylene and having a 3 g/10 minute I<sub>2</sub> melt index, a 0.895 g/cc density and a wide-angle X ray crystallinity of 34 weight percent supplied by Shell Chemical Corporation as a high ethylene content polybutylene polymer under the designation Duraflex DP 8310.

PB2 was a poly(1-butene/ethylene) copolymer having a 2 g/10 minute I<sub>2</sub> melt index and a 0.897 g/cc density supplied by Shell Chemical Corporation as a medium ethylene content polybutylene polymer under the designation Duraflex DP 8220. PB2 was calculated to contain ~5.4 weight percent ethylene and to have a wide-angle X ray crystallinity of ~35 weight percent.

PB3 was a polybutylene polymer having a 1 g/10 minute I<sub>2</sub> melt index and a 0.910 g/cc density supplied by Shell Chemical Corporation as a specially formulated product under the designation Duraflex 1600. PB3 was calculated to contain ~1.5 weight percent ethylene and to have a wide-angle X ray crystallinity of ~50 weight percent.

LDPE was a free-radical initiated, high pressure low density polyethylene having a 8 g/10 minute I<sub>2</sub> melt index, a 0.918 g/cc and a DSC crystallinity of ~44.9 weight percent EVA was a free-radical initiated, high pressure ethylene-vinyl acetate copolymer containing ~18 weight percent vinyl acetate.

Table 12

Heat Seal Strength (lbs./inch)

Sealing Temperature, °C	Inv. Ex 14	Inv. Ex 15	Inv. Ex 16	Inv. Ex 17	Comp. Ex 18	Inv. Ex 19	Inv. Ex 20	Comp. Ex 21	Comp. Ex 22	Comp. Ex 23
75								0.594	0.736	0.476
80			0.480			0.200		1.314	1.640	1.246
85	0.275	1.142	0.866	0.674		0.500	0.500	1.994	2.438	1.542
90	2.588	2.838	2.298	1.590	0.370	0.698	0.826	2.178	2.698	1.816
95			2.596	2.316		1.610	1.358	2.540	2.784	1.742
100	3.472	3.075	2.862	3.294	1.360	3.018	2.192	2.540	2.676	1.720
105			2.874	2.994		2.400	2.978	2.688	3.026	1.936
110	3.796	3.586	2.800	2.556	3.038	2.350	3.138	2.972	3.182	1.782
115			2.840	3.064		3.084	3.272	2.804	3.366	1.890
120	3.834	3.294	3.022	2.912	3.226	3.134	3.016	2.732	3.428	2.550
125			2.852	2.774		3.338	3.494	3.184	3.954	2.438
130	3.540	4.796	3.332	3.296	3.916	3.608	3.840	4.690	5.408	3.562
140	5.880	4.790	3.810	3.880	3.584	4.650	4.390	4.338	6.214	3.118
150	5.702	5.480	4.724	4.646	3.702	5.208	5.050			
Median <sub>90-140°C</sub>	3.668	3.440	2.857	2.953	3.132	3.051	3.077	2.768	3.274	1.913
Average Deviation <sub>90-140°C</sub>	0.676*	0.709*	0.276	0.447	1.145*	0.820	0.835	0.602	0.911	0.529
% Average Deviation	18.4%	20.6%	9.6%	15.1%	36.6%	26.9%	27.1%	21.8%	27.8%	27.7%
Median <sub>100-130°C</sub>	3.67	3.44	2.86	2.99	3.13	3.08	3.14	2.80	3.37	1.94
Average Deviation <sub>100-130°C</sub>	0.155	0.554	0.135	0.203	0.763	0.352	0.346	0.486	0.631	0.499
% Average Deviation	4.2%	16.1%	4.7%	6.8%	24.3%	11.4%	11.0%	17.3%	18.7%	25.8%

\*<sub>n</sub> = 6 for the average deviation computation.

**Table 13**  
7 Day Hot Tack Strength (Newtons/inch)

Sealing Temperature, °C	Inv. Ex 14	Inv. Ex 15	Inv. Ex 16	Comp. Ex 18	Inv. Ex 19
65					0.925
70	0.217				1.694
75	1.215	0.543		0.221	2.735
80	6.147	6.310	0.694	3.645	3.730
85	6.882	6.717	1.871	5.685	5.088
90	6.969	7.336	4.961	6.477	5.415
95	7.076	7.502	5.981	6.203	5.748
100	7.304	7.119	5.966	6.147	4.734
105	7.406	7.220	5.162	5.887	5.687
110	7.709	7.300	5.574	5.844	5.617
115	7.310	7.062	4.770	6.273	5.277
120	7.748	6.938	5.397	6.539	5.185
125	6.804	6.033	4.737	5.081	4.105
130	4.841	3.614	4.002	4.210	3.790
140	2.938	2.452	2.410	2.532	2.669
150	2.354	2.374	2.098	2.441	1.896
Median <sub>10-140°C</sub>	7.190	7.091	5.062	6.017	5.231
Average Deviation <sub>140°C</sub>	1.0884	1.33476	0.733	0.94698	0.79856
%Average Deviation	15.1%	18.8%	14.5%	15.7%	15.3%

**Table 14**  
Sealant-to-Sealant Kinetic COF

Days After Film Fabrication	Inv. Ex 14	Inv. Ex 15	Inv. Ex 16	Comp. Ex 18	Comp. Ex 19
1	0.976	1.0152	0.2856	0.9176	1.3648
2	2.00	1.2434	0.2692	0.7386	1.4592
7	0.251	0.2708	0.2446	0.1346	1.576
14			0.2506		1.3502
15	0.191	0.1856		0.1184	

**Table 15**

Film Abuse Properties

Days	Inv. Ex 14	Inv. Ex 15	Comp. Ex 18
Puncture [ft.-lbs./in <sup>3</sup> ]	48.65	54.1	43.45
Elmendorf			
Tear (MD) [grams]	20.4	30.0	25.0
Elmendorf			
Tear (CD) [grams]	657.0	1175.7	683.1

The results in FIG. 19-21 and Tables 12-15 indicate that Inventive Examples 14, 15, 16 and 19 are characterized by excellent sealing properties. The blend ratios of sealant base resin to LDPE carrier resin for Inventive Examples 14, 15 and 16/17 were nil, 1:0.39, 1:0.556, and 1:0.125, respectively. Inventive Examples 14 demonstrated that excellent peelable seal performance can be obtained with a high ethylene content polybutylene polymer and without the use of low density polyethylene (LDPE) or any other polymer as a so-called incompatibilizer. Inventive Examples 15 and 19 which comprised LDPE carrier resin demonstrated that excellent performance can be obtained without the use of excessive quantities of an incompatibilizer. This result same was also obtained for Inventive Examples 1, 2 and 8 wherein the LDPE carrier resin only constituted 7.2 weight percent of the respective compositions. Inventive Example 19 demonstrated that both silicon and amide slip additive are suitable in the present invention.

However, Inventive Example 16 was an especially preferred inventive example because it exhibited smooth and consistent sealing performance throughout the sealing temperature ranges of 100°-130°C and 90°-140°C as well as exceptional COF performance. FIG. 18 and 19 indicate that this inventive example had a broad sealing window plateau whether the defined heat seal strength was 1.8-3.2 lbs./inch (0.32-0.57 kg/cm) or, alternately, 2.4-3.8 lbs./inch (0.43-0.68 kg/cm). Also, as shown in FIG. 20, desirably Inventive Example 16 did not show an initial increase in its COF (as was the case for Inventive Examples 14 and 15) and maintained a desirably low and stable COF up to 15 days after film fabrication.

The smooth, uniform performance of Inventive Example 16 was surprising and unexpected. That is, although the blend ratio of carrier resin to sealant base resin was 42 percent higher for Inventive Example 16 (as compared to, for example, Inventive Example 15), Inventive Example 16

exhibited none of the performance inconsistencies foretold by De Clippeleir. In this connection, it was important to recognize that the carrier resin to sealant base resin blend ratio for Inventive Example 15 (that is, 0.3904:1) was substantially equivalent to that of the so-called excellent performing 51percent mPE:29percent PB:20percent LDPE formulation disclosed by De Clippeleir (that is, 0.3922:1) and as such Inventive Example 16 comprised substantially more polybutylene polymer and substantially more of an incompatibilizer than the De Clippeleir formulation.

Further, the sensory evaluations indicated that there was substantially less off-taste contribution associated with inventive examples based on homogeneously branched ethylene polymers relative to comparative example 21 which was representative incumbent EVA/polybutylene formulations.

We Claim

1. A sealant composition comprising

a) as a sealant base resin, at least one  
5 homogeneously branched ethylene polymer characterized by a  
lack of a polymer fraction having a degree of short chain  
branching less than or equal to 2 methyls/1000 carbons and  
greater than or equal to 30 methyls/1000 carbons, as  
determined using a temperature rising elution fractionation  
10 and infrared (IR) technique,

b) at least 25 weight percent, based on the  
total weight of the composition, of at least one polybutylene  
polymer having a crystallinity less than 36 weight percent,  
based on the total weight of the polymer, as determined using  
15 wide-angle X ray,

c) greater than 0.5 weight percent, based on  
the total weight of the composition, of at least one slip  
additive, and

d) at least 0.5 weight percent, based on the  
20 total weight of the composition, of at least one silica-  
containing or calcium-containing additive,

wherein the composition, when fabricated into a  
sealant layer having a thickness of from 0.28 to 0.3 mil  
(0.0071 to 0.0076 mm), is characterized as having:

25 (i) a heat seal initiation  
performance, wherein after the layer is aged  
for less than or equal to 192 hours at 22-23°C  
and 50 percent relative humidity, the layer  
has a heat seal strength in the range of from  
30 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm)  
width at a sealing temperature of 100°C, and  
(ii) a median heat seal strength in  
the range of from 2.6 to 4.0 lbs./inch (0.46  
to 0.71 kg/cm) width for sealing temperatures  
35 from 100° to 130°C,



wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25 cm/minute).

2. The composition of Claim 1 wherein the homogeneously branched ethylene polymer is a substantially linear ethylene interpolymer characterized as having:

(a) melt flow ratio,  $I_{10}/I_2 \geq 5.63$ ,

(b) a molecular weight distribution,  $M_w/M_n$ , as determined by gel permeation chromatography and defined by the equation:

$$(M_w/M_n) \leq (I_{10}/I_2) - 4.63,$$

(c) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene polymer, wherein the substantially linear ethylene polymer and the linear ethylene polymer comprise the same comonomer or comonomers, the linear ethylene polymer has an  $I_2$  and  $M_w/M_n$  within ten percent of the substantially linear ethylene polymer and wherein the respective critical shear rates of the substantially linear ethylene polymer and the linear ethylene polymer are measured at the same melt temperature using a gas extrusion rheometer, and

(d) a single differential scanning calorimetry, DSC, melting peak between  $-30^\circ$  and  $150^\circ\text{C}$ .

3. The composition of Claim 1 wherein the homogeneously branched ethylene polymer is a linear ethylene interpolymer.

5 4. The composition of Claim 3 wherein the homogeneously branched linear ethylene polymer is characterized as having a single differential scanning calorimetry, DSC, melting peak between  $-30^{\circ}$  and  $150^{\circ}\text{C}$ .

10 5. The composition of Claim 1 wherein the weight percent of the at least one polybutylene polymer is in the range of from 28 to 73, based on the total weight of the composition.

15 6. The composition of Claim 1 wherein the at least one polybutylene polymer has a crystallinity less than or equal to 35 weight percent based on the total weight of the polymer, as determined using wide-angle X ray.

20 7. The composition of Claim 6 wherein the at least one polybutylene polymer has a crystallinity in the range of from 0 to 35 weight percent based on the total weight of the polymer, as determined using wide-angle X ray.

25 8. The composition of Claim 1 wherein the at least one polybutylene polymer has a density of less than or equal to 0.896 g/cc, as determined in accordance with ASTM D792.

30 9. The composition of Claim 8 wherein the at least one polybutylene polymer has a density in the range of from 0.862 g/cc to 0.896 g/cc, as determined in accordance with ASTM D792.

35 10. The composition of Claim 1 wherein the at least one polybutylene polymer is a polymer selected from the

group consisting of a poly(1-butene/hexene) copolymer, poly(1-butene/pentene) copolymer, poly(1-butene/ethylene) copolymer, poly(1-butene/propylene) copolymer, and poly(1-butene/ethylene/propylene) terpolymer.

5

11. The composition of Claim 1 wherein the at least one polybutylene polymer is a poly(1-butene/ethylene) copolymer.

10

12. The composition of Claim 11 wherein the poly(1-butene/ethylene) copolymer has an ethylene content greater than 5.4 weight percent, based on the total weight of the copolymer.

15

13. The composition of Claim 11 wherein the poly(1-butene/ethylene) copolymer has an ethylene content in the range of from 5.6 to 15.8 weight percent, based on the total weight of the copolymer.

20

14. The composition of Claim 11 wherein the poly(1-butene/ethylene) copolymer has an ethylene content greater than 6 weight percent, based on the total weight of the copolymer.

25

15. The composition of Claim 6 wherein the at least one polybutylene polymer is further characterized as having a ring and ball softening point greater than or equal to 108°C, as determined in accordance with ASTM E28.

30

16. The composition of Claim 1 wherein the composition further comprises an olefin polymer as an optional additive concentrate carrier resin.

17. The composition of Claim 16 wherein the optional olefin polymer is an ethylene polymer.

35

18. The composition of Claim 17 wherein the ethylene polymer is characterized as having long chain branches.

5 19. The composition of Claim 18 wherein the ethylene polymer having long chain branches is a low density polyethylene (LDPE) or a homogeneously branched substantially linear ethylene polymer.

10 20. The composition of Claim 16 wherein the optional olefin polymer has a weight percent crystallinity which is higher than the weight percent crystallinity of the sealant base resin.

15 21. The composition of Claim 16 wherein the optional olefin polymer has a weight percent crystallinity which is at least 35 percent higher than the weight percent crystallinity of the sealant base resin.

20 22. The composition of Claim 1 wherein the weight percent of the at least one slip additive is in the range of from 0.8 to 1.2, based on the total weight of the composition.

25 23. The composition of Claim 1 wherein the at least one slip additive is a secondary amide.

24. The composition of Claim 23 wherein the secondary amide is selected from the group consisting of  
30 oleyl palmitamide, stearyl erucamide, erucyl erucamide, oleyl oleamide, erucyl stearamide, ethylene bis-stearamide, and ethylene bis-oleamide.

25. The composition of Claim 23 wherein the  
35 secondary amide is oleyl palmitamide.

26. The composition of Claim 23 wherein the secondary amide is erucyl stearamide.

27. The composition of Claim 23 wherein the  
5 secondary amide is stearyl erucamide.

28. The composition of Claim 1, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as  
10 having a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C.

15

29. The composition of Claim 1, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is further characterized as having (iv) a heat seal strength average  
20 deviation of less than or equal to 16.5 percent for sealing temperatures from 100° to 130°C.

30. The composition of Claim 1, when fabricated into a sealant layer having a thickness of from  
25 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is further characterized as maintaining the characteristic defined in (iii) after aging at 22-23°C and 50 percent relative humidity for 528 hours following fabrication of the layer.

30 31. The composition of Claim 1, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil, is characterized as having a heat sealing window plateau of greater than or equal to 20°C for a defined heat seal strength of 1.8-3.2 lbs./inch (0.32 to 0.57 kg/cm)

width after aging at 22-23°C and 50 percent relative humidity for at least 528 hours following fabrication of the layer.

32. The composition of Claim 1, when  
5 fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil, is characterized as having a heat sealing window plateau of greater than or equal to 25°C for a defined heat seal strength of 1.8-3.2 lbs./inch width after aging at 22-23°C and 50 percent relative humidity (0.32 to 0.57 kg/cm)  
10 for at least 528 hours following fabrication of the layer.

33. The composition of Claim 1, when  
fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as  
15 having a heat sealing window plateau of greater than or equal to 30°C for a defined heat seal strength of 1.8-3.2 lbs./inch (0.32 to 0.57 kg/cm) width after aging at 22-23°C and 50 percent relative humidity for at least 528 hours following fabrication of the layer.

20

34. The composition of Claim 1, when  
fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as  
having a heat sealing window plateau of greater than or equal  
25 to 35°C after aging at 22-23°C and 50 percent relative humidity for at least 528 hours following fabrication of the layer.

35. A film having at least one sealant layer,  
30 the at least one sealant layer comprising

a) as a sealant base resin, at least one  
homogeneously branched ethylene polymer characterized by a  
lack of a polymer fraction having a degree of short chain  
branching less than or equal to 2 methyls/1000 carbons and  
35 greater than or equal to 30 methyls/1000 carbons , as

determined using a temperature rising elution fractionation and infrared (IR) technique,

b) at least 25 weight percent, based on the total weight of the layer, of at least one polybutylene polymer having a crystallinity less than 36 weight percent, based on the total weight of the polymer, as determined using wide-angle X ray,

c) greater than 0.5 weight percent, based on the total weight of the layer, of at least one slip additive, and

d) at least 0.5 weight percent, based on the total weight of the layer, of at least one silica-containing or calcium-containing additive,

wherein the sealant layer at a thickness of from 0.28 to 0.3 mil is characterized as having:

(i) a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

(ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.275 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25 cm/minute).

36. A method for making a peelable seal film or coating structure having at least two layers, the method comprising the steps of:

(i) feeding a first polymer

composition into a sealant layer coextrusion extruder,

(ii) feeding a second polymer composition into a skin layer coextrusion extruder,

(iii) optionally feeding a polymer composition into a core or structural layer coextrusion extruder,

(iv) melting and mixing the polymer compositions at melt temperatures above their melting points to form at least two molten polymer streams,

(vi) extruding the molten polymer streams through a coextrusion feedblock into a die to form a web or a tube comprising a sealant layer and a skin layer,

(vii) blowing up and cooling the tube or drawing down and cooling the web to form the peelable seal film or coating structure, and

(viii) collecting the film or coating structure,

the method wherein the first polymer composition comprises

a) as a sealant base resin, at least one homogeneously branched ethylene polymer characterized by a lack of a polymer fraction having a degree of short chain branching less than or equal to 2 methyls/1000 carbons and greater than or equal to 30 methyls/1000 carbons, as determined using a temperature rising elution fractionation and infrared (IR) technique,

b) at least 25 weight percent, based on the total weight of the composition, of at least one polybutylene polymer having a crystallinity less than 36 weight percent, based on the total weight of the polymer, as determined using wide-angle X ray,



c) greater than 0.5 weight percent, based on the total weight of the composition, of at least one slip additive, and

d) at least 0.5 weight percent, based on the total weight of the composition, of at least one silica-containing or calcium-containing additive,

wherein the first polymer composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as having:

(ix) a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

(x) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.275 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25 cm/minute).

37. A film or coated structure comprising at least one sealant layer and at least one additional film layer wherein the additional film layer is selected from the group consisting of a polyamide, polyethylene, polypropylene, polyester, polyvinylidene chloride and polycarbonate and the sealant layer comprises

a) as a sealant base resin, at least one homogeneously branched ethylene polymer characterized by a lack of a polymer fraction having a degree of short chain

branching less than or equal to 2 methyls/1000 carbons and greater than or equal to 30 methyls/1000 carbons , as determined using a temperature rising elution fractionation and infrared (IR) technique,

5                   b)           at least 25 weight percent, based on the total weight of the layer, of at least one polybutylene polymer having a crystallinity less than 36 weight percent, based on the total weight of the polymer, as determined using wide-angle X ray,

10                   c)           greater than 0.5 weight percent, based on the total weight of the layer, of at least one slip additive, and

                  d)           at least 0.5 weight percent, based on the total weight of the layer, of at least one silica-containing  
15 or calcium-containing additive,

                  wherein the sealant layer at a thickness of from 0.28 to 0.3 mil is characterized as having:

                  (i) a heat seal initiation  
20                   performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

25                   (ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch width for sealing temperatures from 100° to 130°C,

                  wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.275 MPa)  
30                   sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25 cm/minute).

37.           A peelable seal sealant composition  
35           comprising

a) as a sealant base resin, at least one ethylene polymer,

b) at least 25 weight percent, based on the total weight of the composition, of at least one polybutylene polymer,

c) greater than 0.5 weight percent, based on the total weight of the composition, of at least one slip additive, and

d) at least 0.5 weight percent, based on the total weight of the composition, of at least one silica-containing or calcium-containing additive,

wherein the composition, when fabricated into a sealant layer having a thickness of from 0.28 to 0.3 mil (0.0071 to 0.0076 mm), is characterized as having:

(i) a heat seal initiation performance, wherein after the layer is aged for less than or equal to 192 hours at 22-23°C and 50 percent relative humidity, the layer has a heat seal strength in the range of from 1.5 to 3.5 lbs./inch (0.27 to 0.64 kg/cm) width at a sealing temperature of 100°C, and

(ii) a median heat seal strength in the range of from 2.6 to 4.0 lbs./inch (0.46 to 0.71 kg/cm) width for sealing temperatures from 100° to 130°C,

wherein heat sealing is accomplished using a heat sealer set at a 0.5 second dwell time and 40 psi (0.275 MPa) sealing jaw pressure and heat seal strengths are determined by a T-peel test using a tensiometer set at a crosshead speed of 10 inches/minute (25 cm/minute).

38. The composition of Claim 37 wherein the at least one sealant base resin is a low density polyethylene resin.

39. The composition of Claim 37 wherein the at least one sealant base resin is a homogeneously branched linear ethylene interpolymer.

5 40. The composition of Claim 37 wherein the at least one sealant base resin is a homogeneously branched substantially linear ethylene interpolymer.

10 41. The composition of Claim 37 wherein a homogeneously branched ethylene polymer is employed as at least one optional incompatibilizer or concentrate carrier resin.

15 42. The composition of Claim 41 wherein the homogeneously branched ethylene polymer is a homogeneously branched linear ethylene interpolymer.

20 43. The composition of Claim 41 wherein the homogeneously branched ethylene polymer is a homogeneously branched substantially linear ethylene interpolymer.

25 44. The composition of Claim 37 wherein a low density polyethylene resin is employed as at least one optional incompatibilizer or concentrate carrier resin.

30 45. The composition of Claim 37 wherein an optional incompatibilizer or concentrate carrier resin is employed which is characterized as having a weight percent crystallinity that is at least 35 percent higher than the weight percent crystallinity of the sealant base resin.

FIG.1

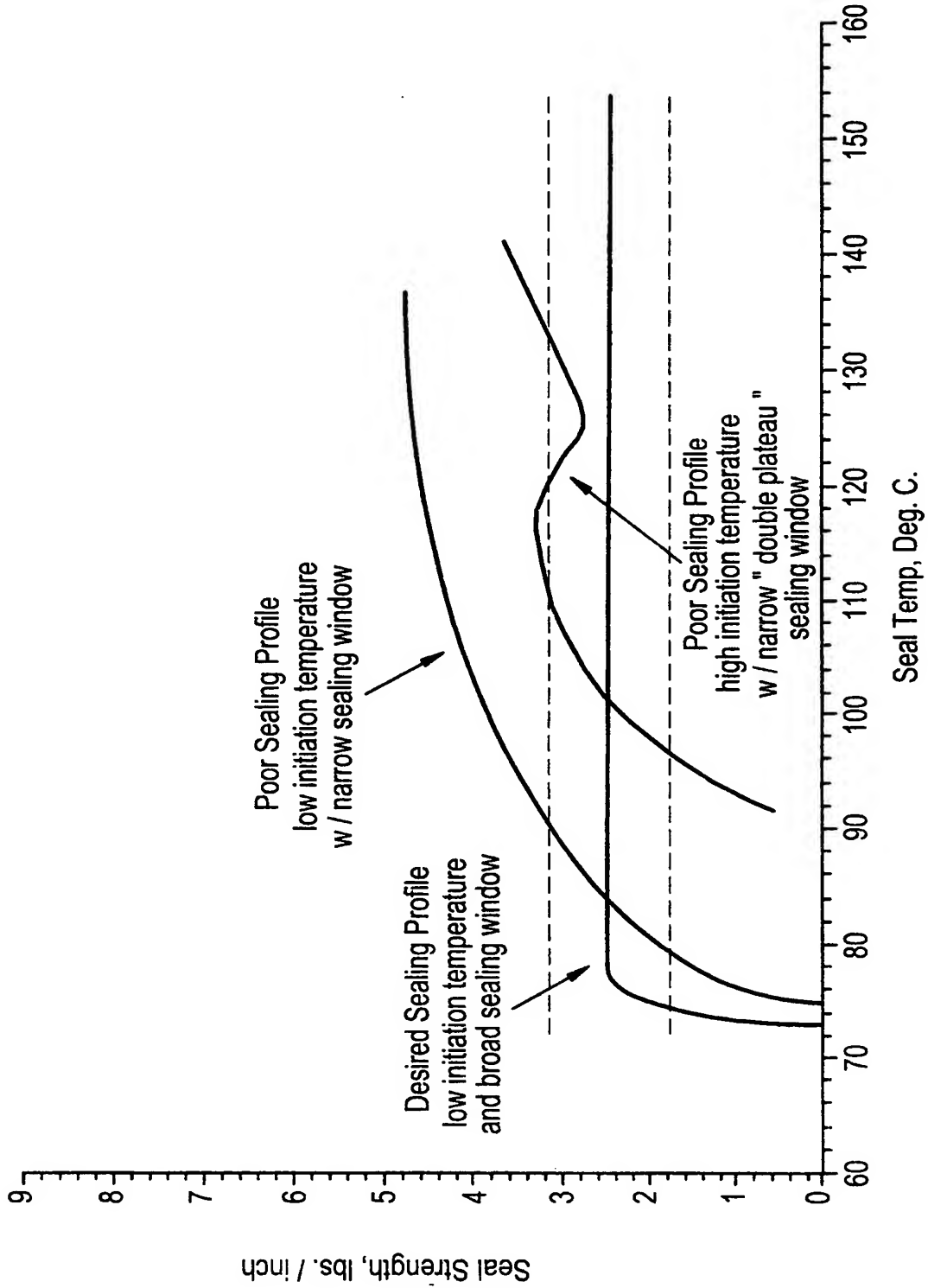


FIG.2

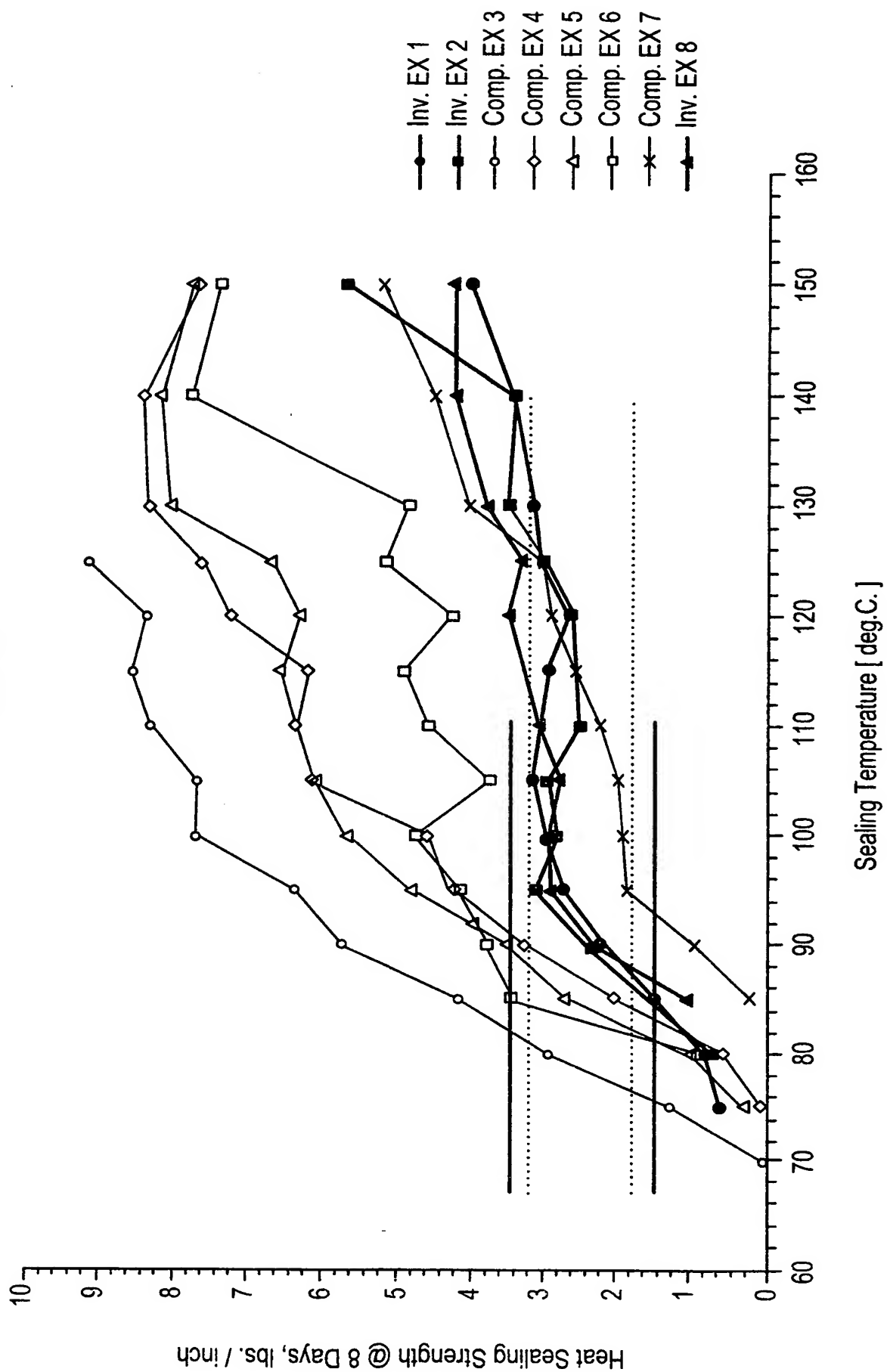


FIG.3

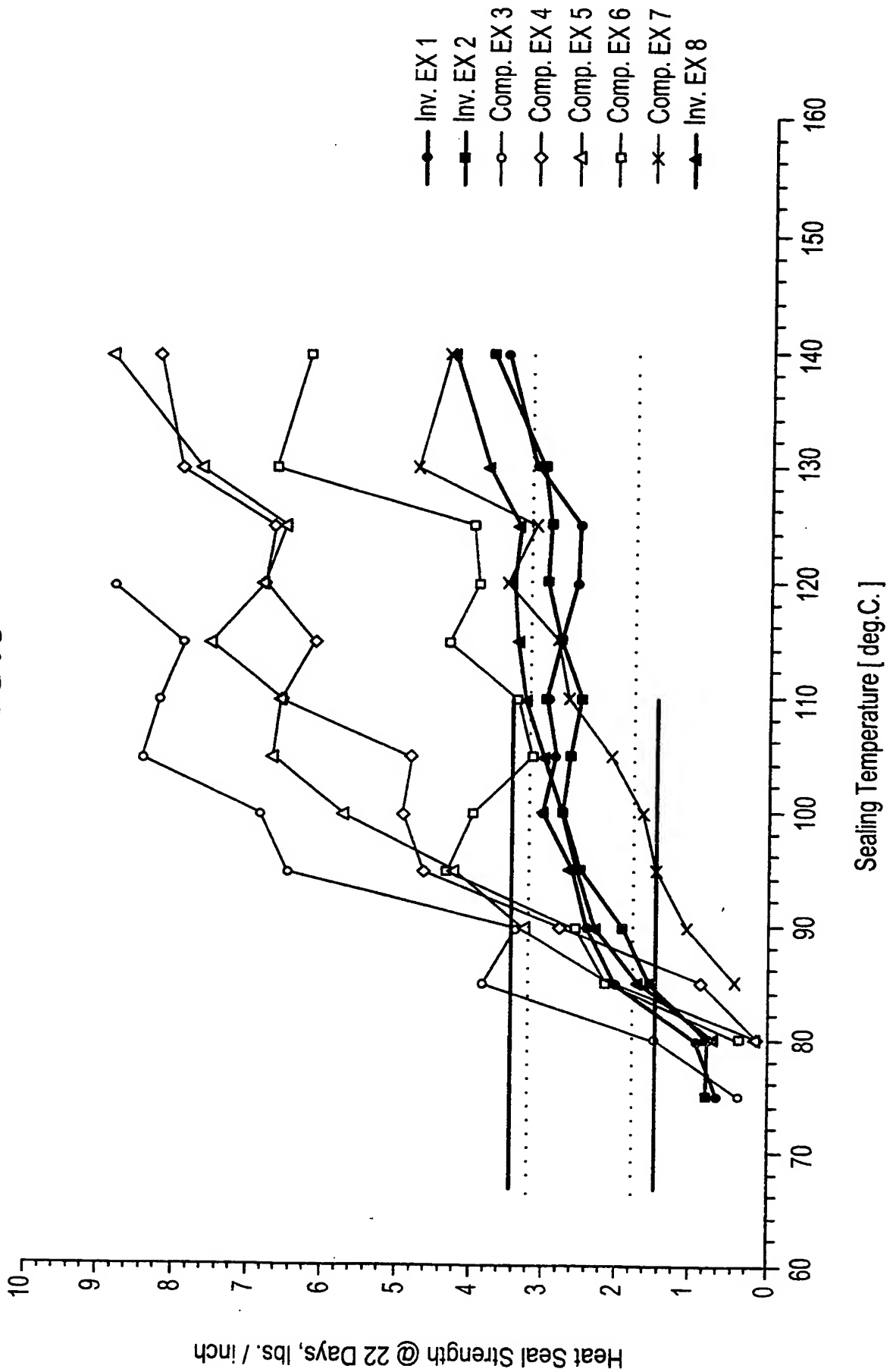


FIG.4

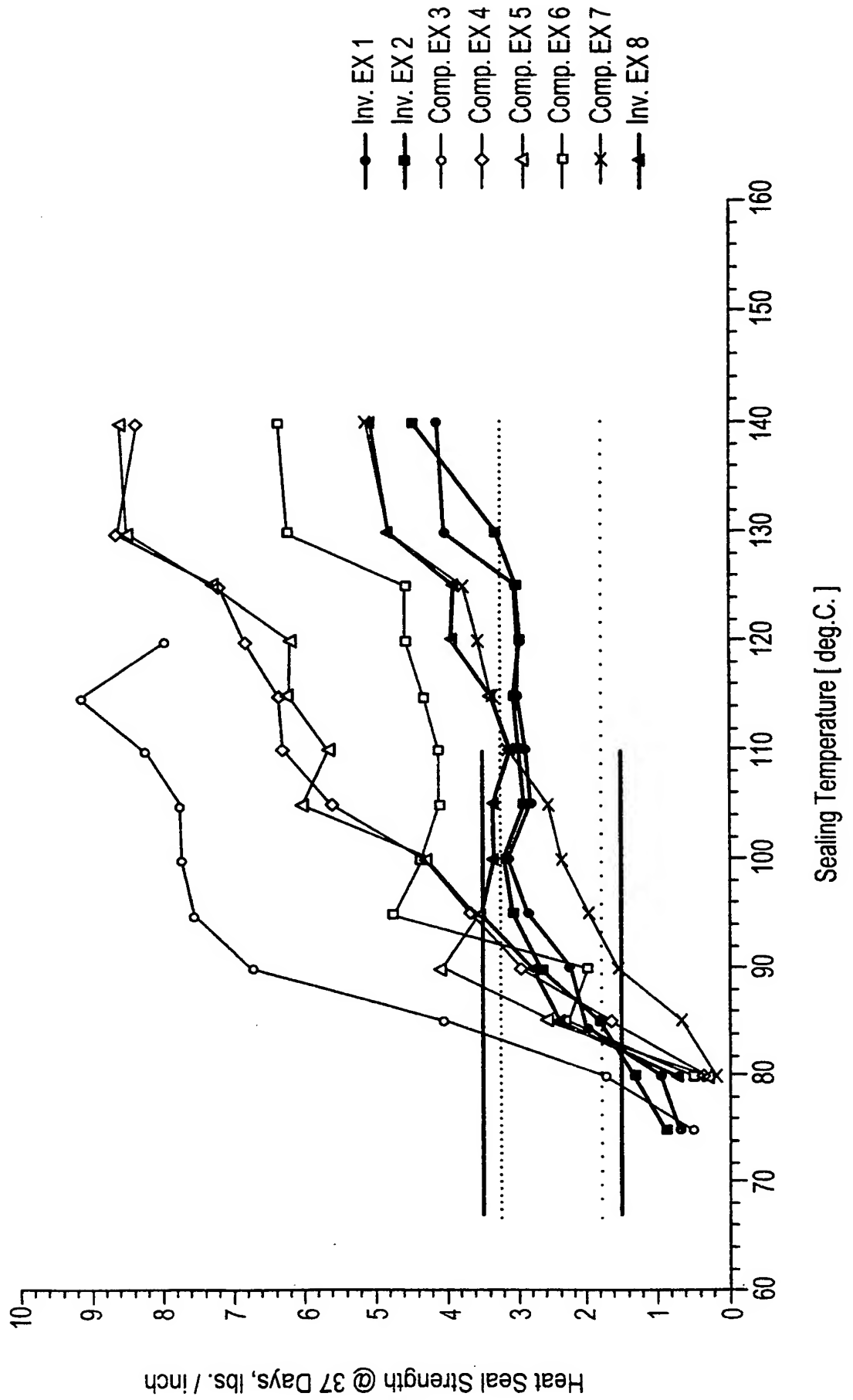




FIG.5

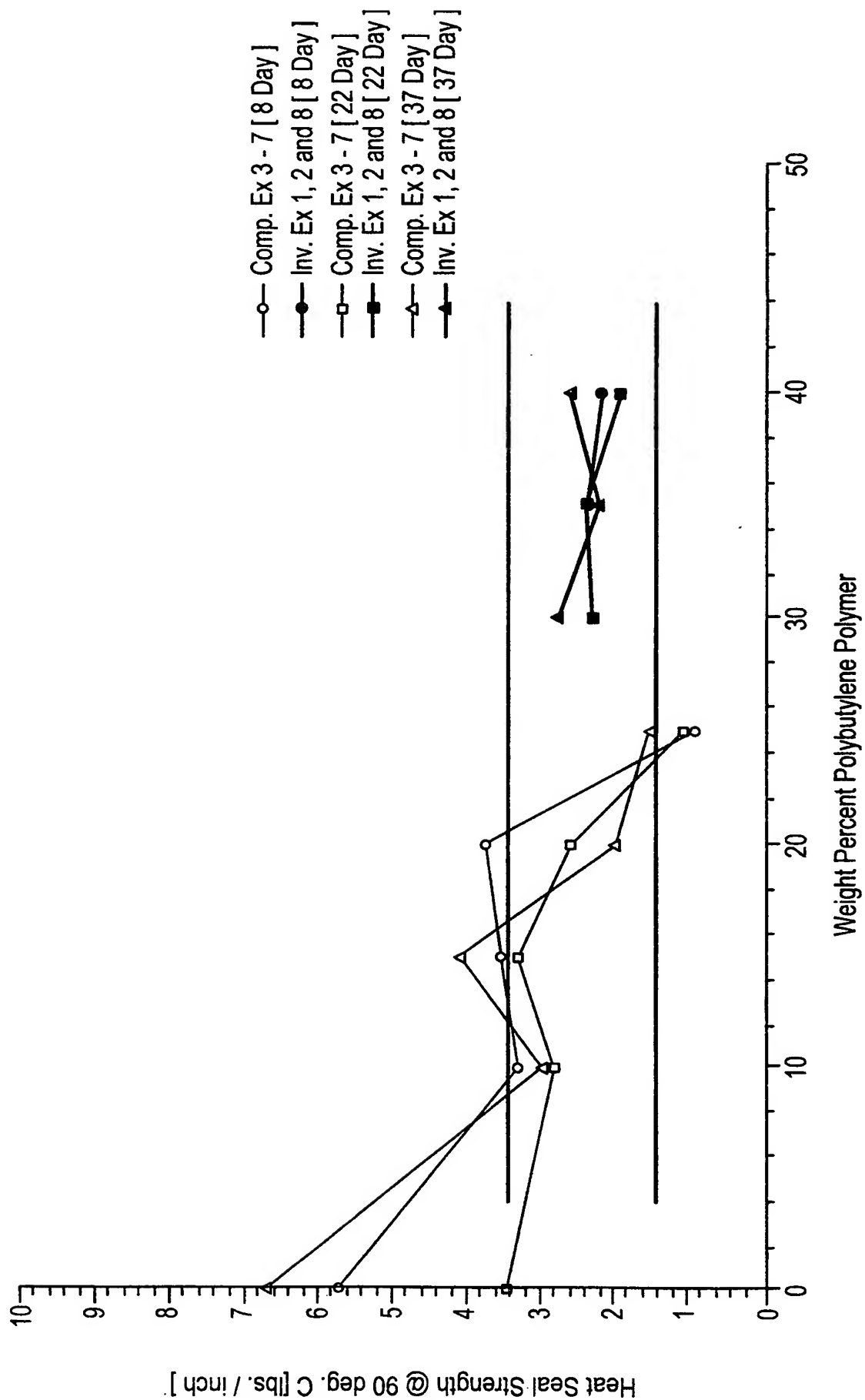


FIG.6

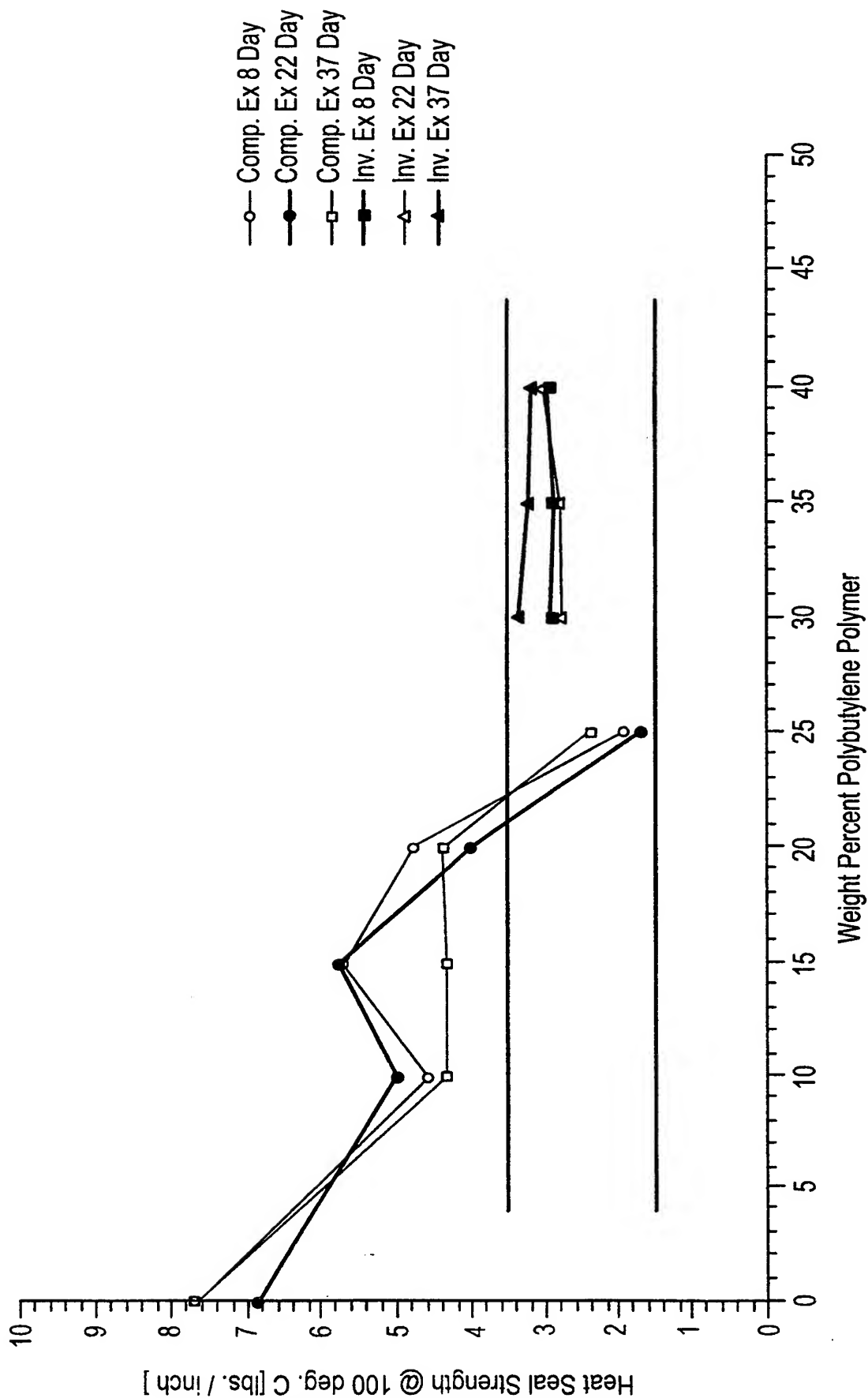


FIG. 7

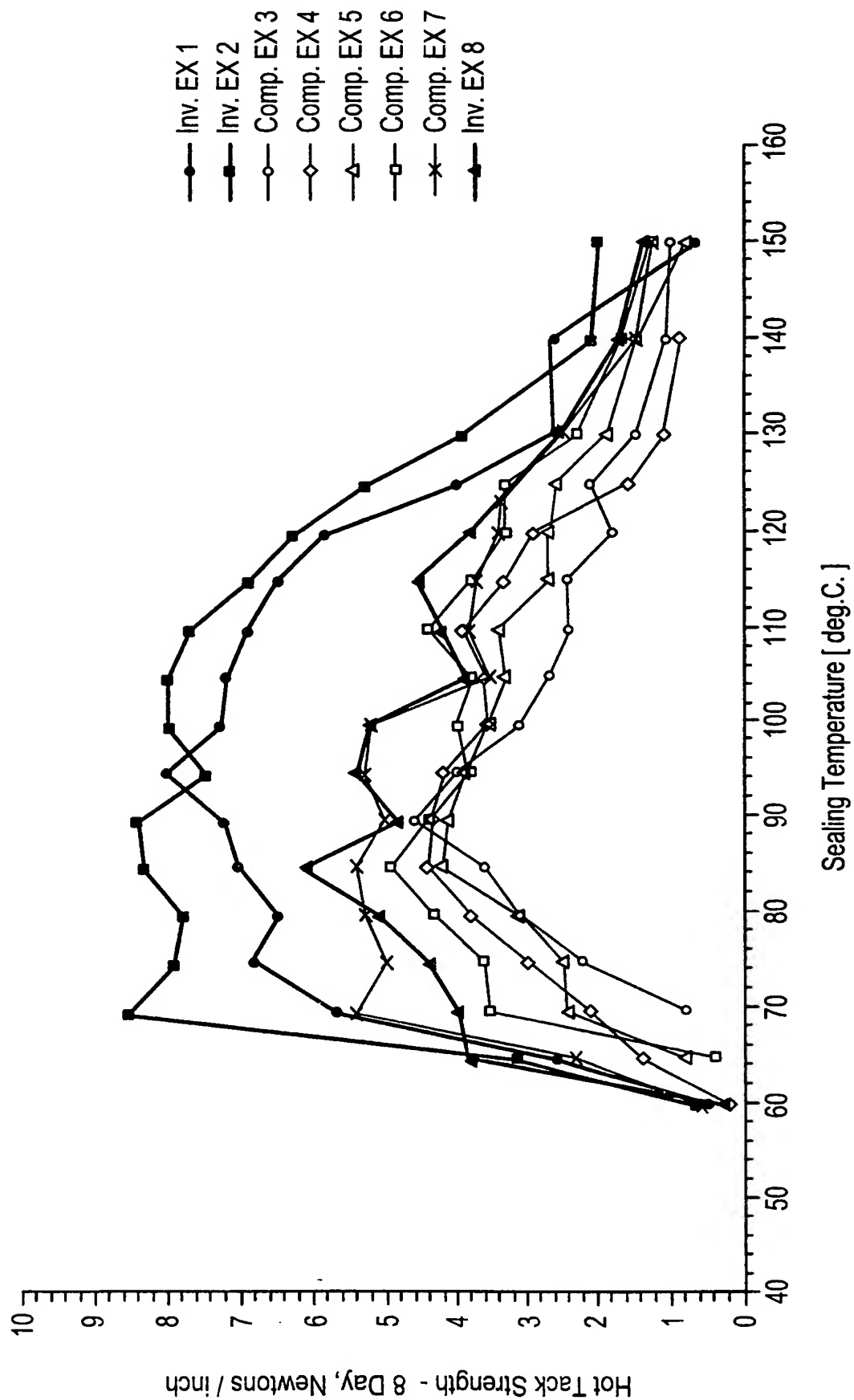


FIG.8

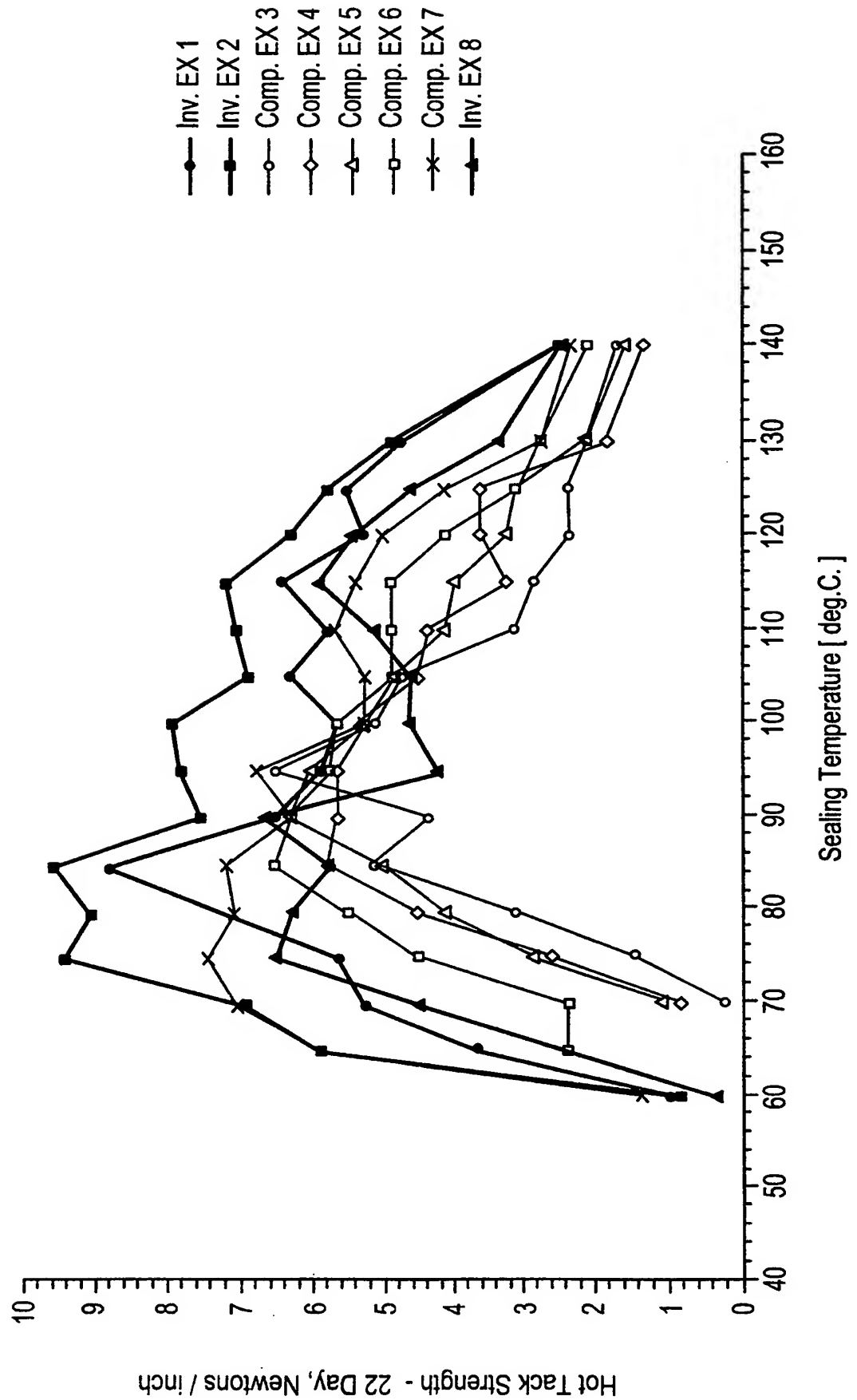


FIG.9

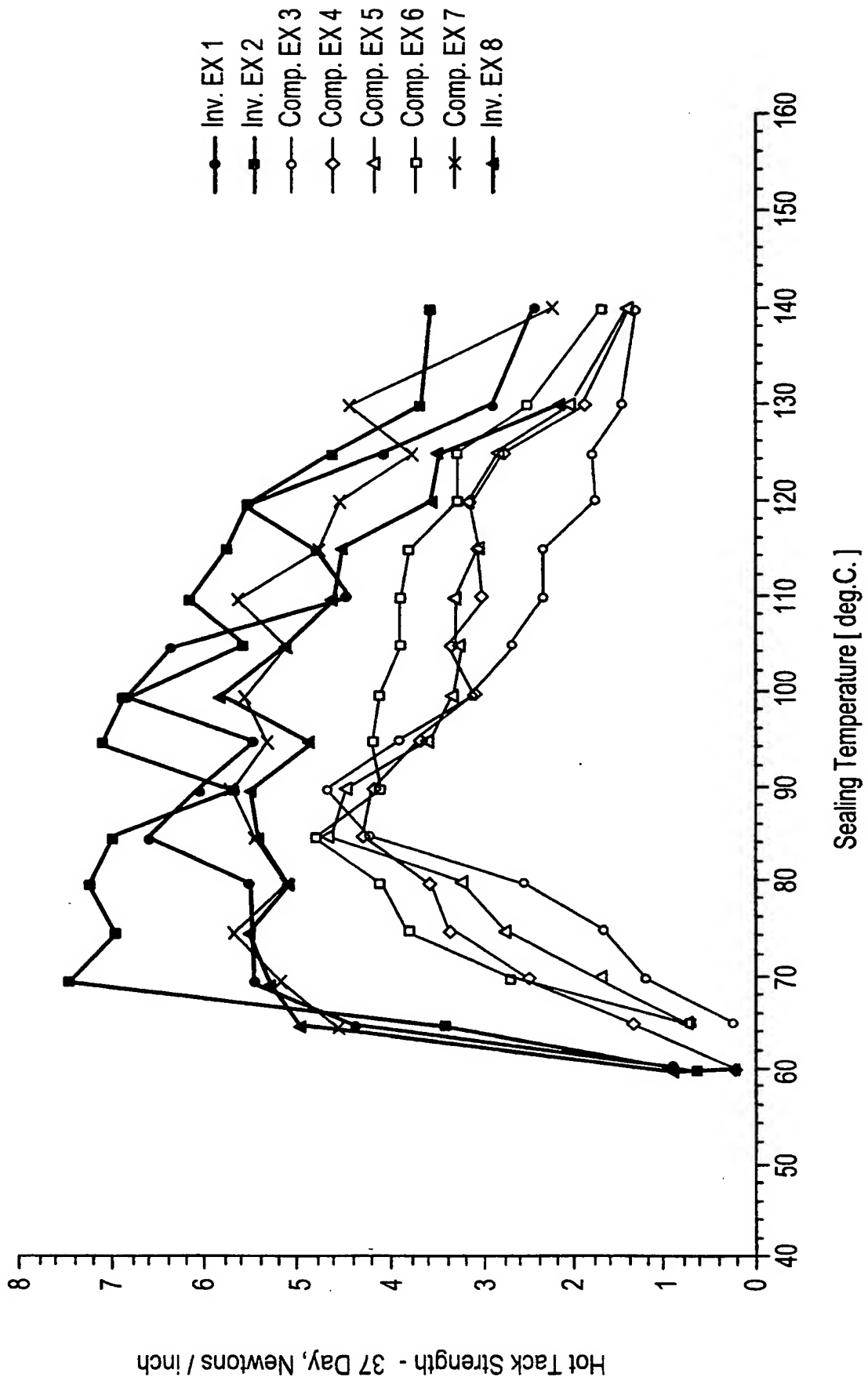


FIG.10

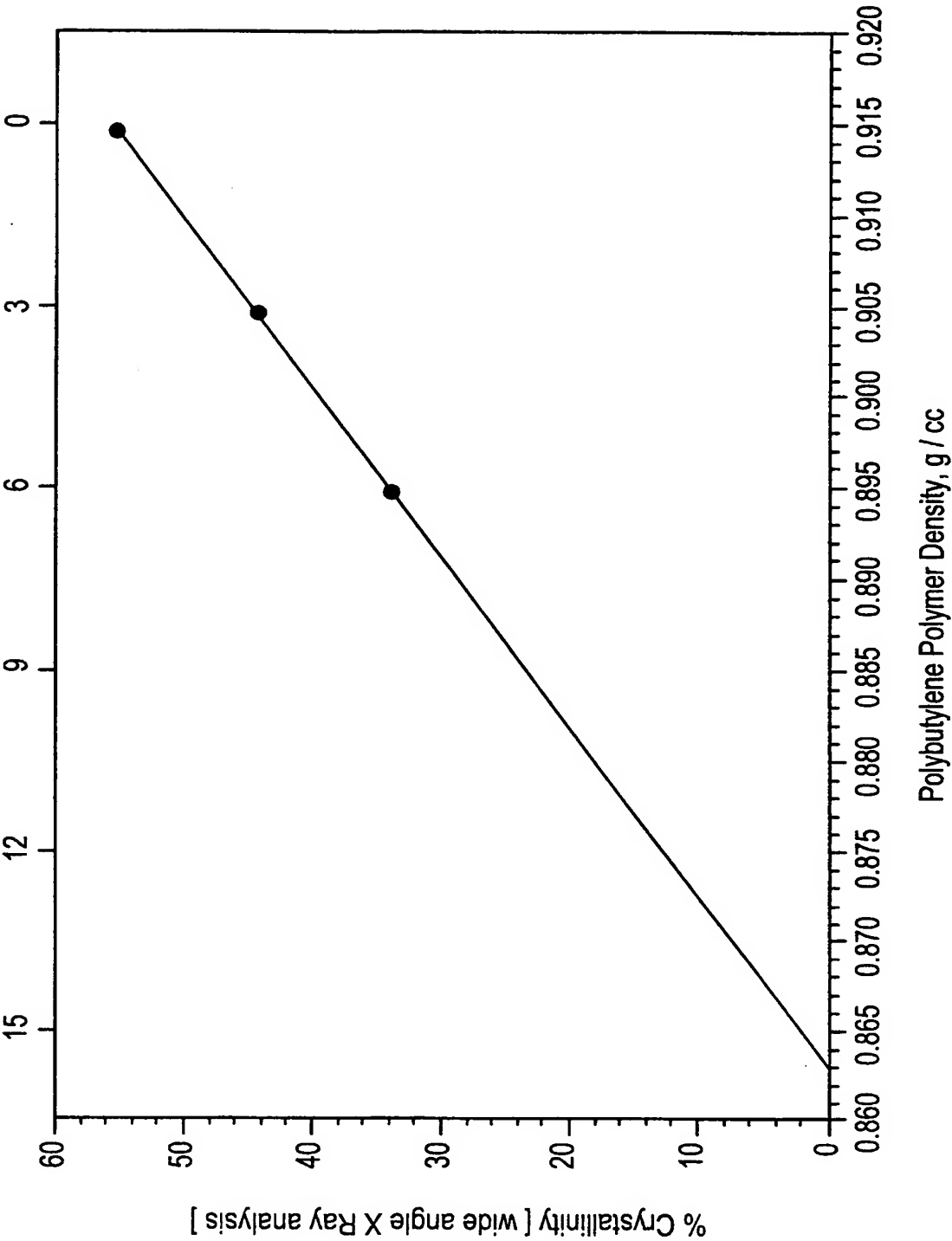


FIG.11

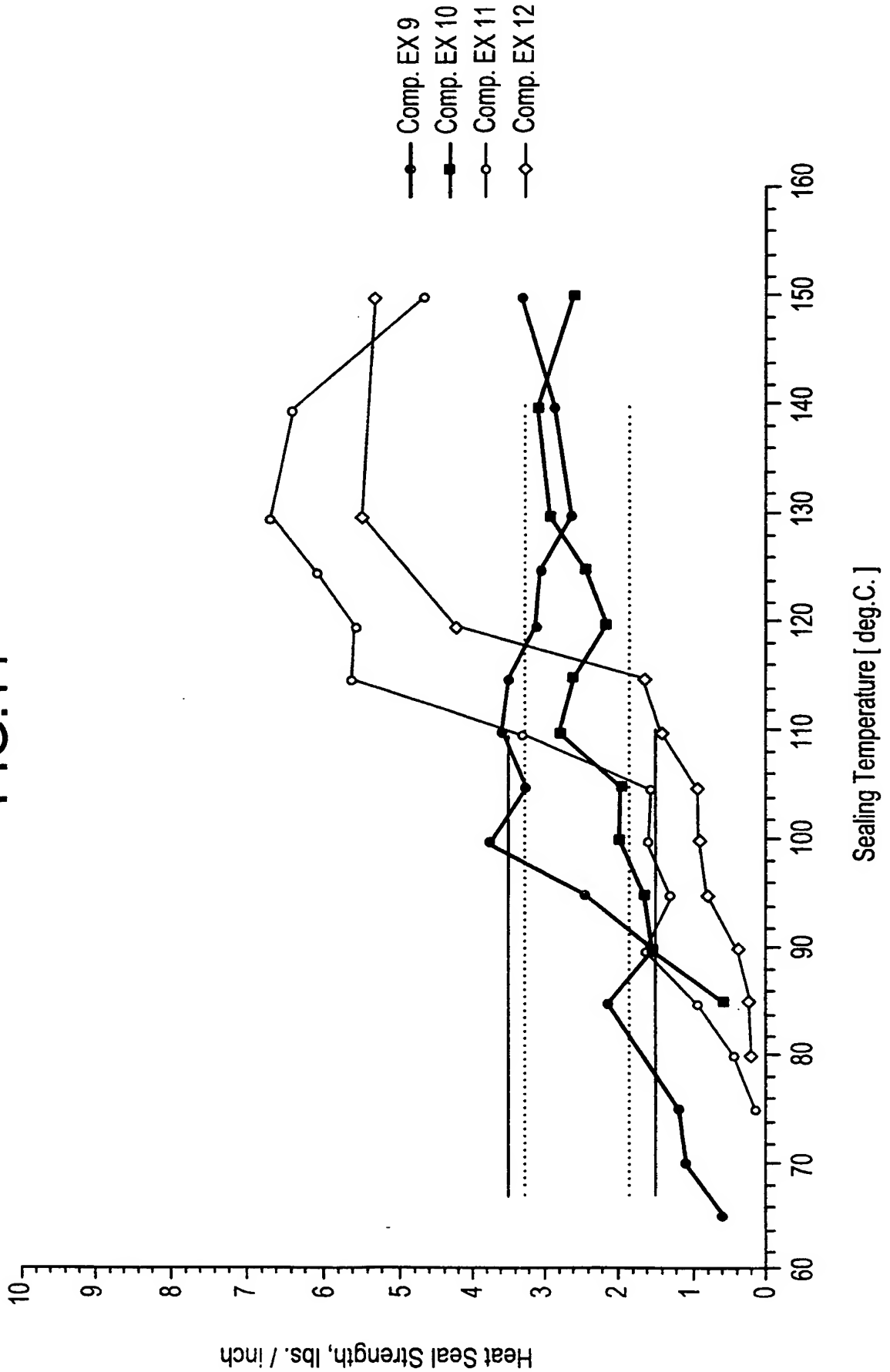


FIG. 12

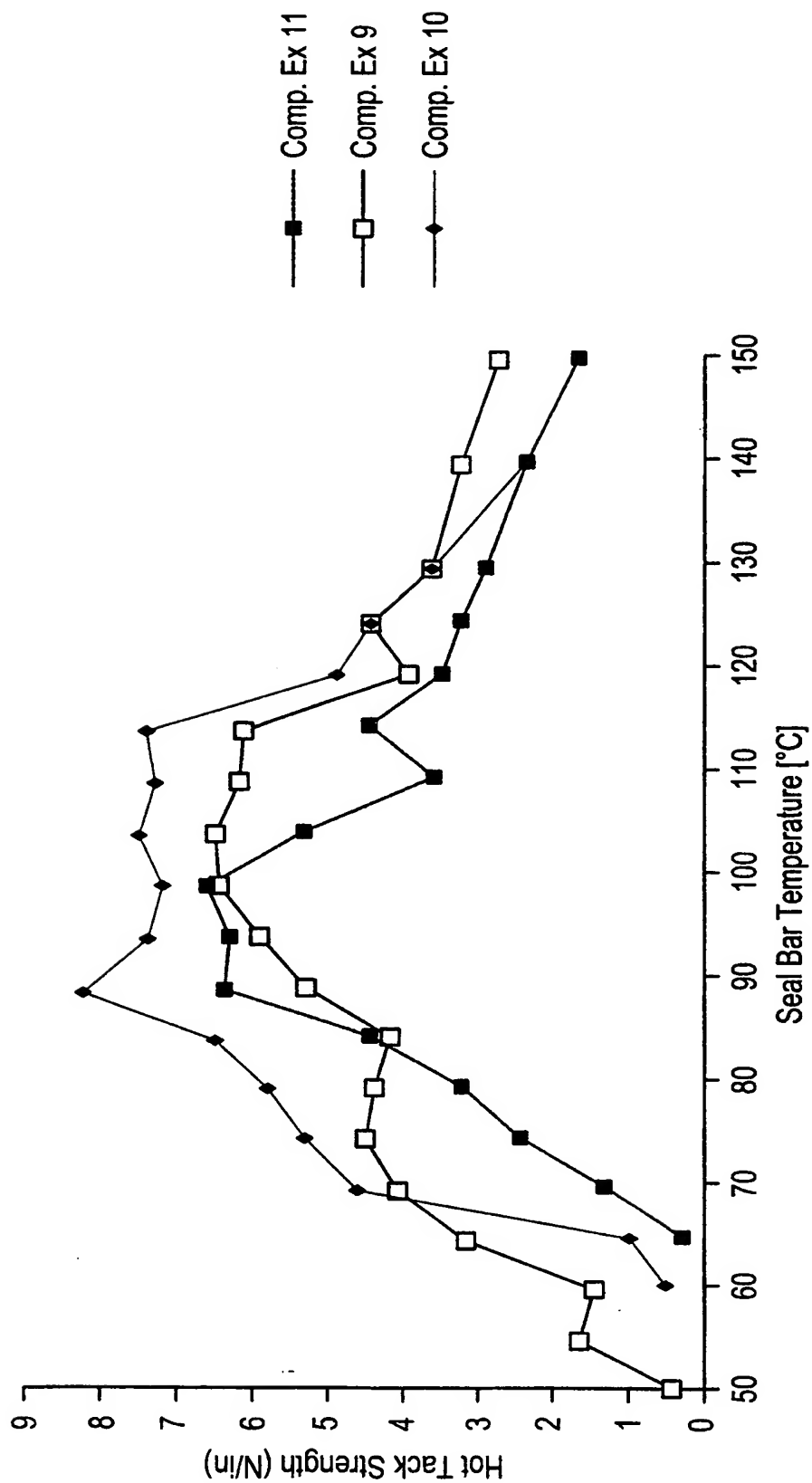




FIG. 13

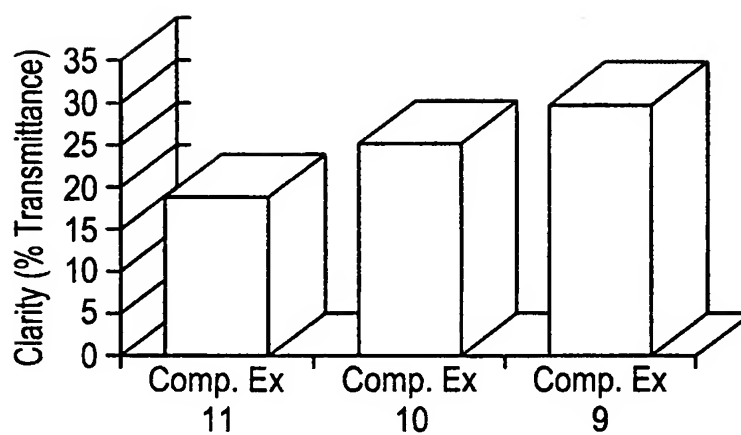


FIG. 14

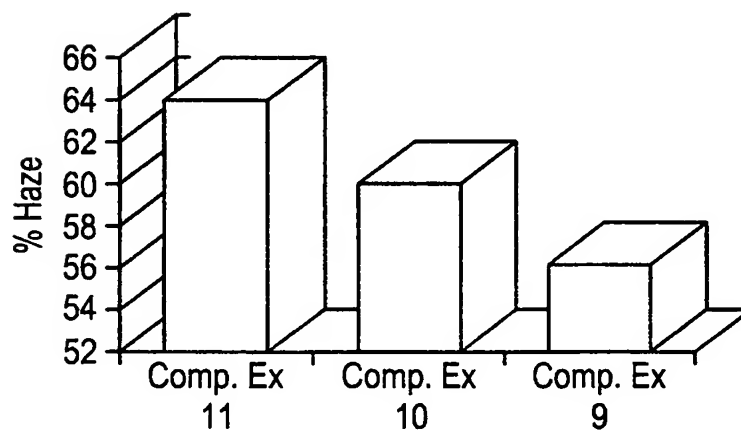


FIG. 15

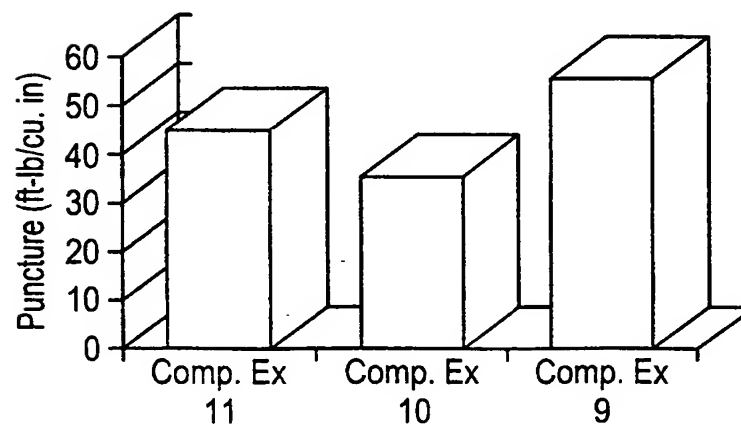


FIG. 16

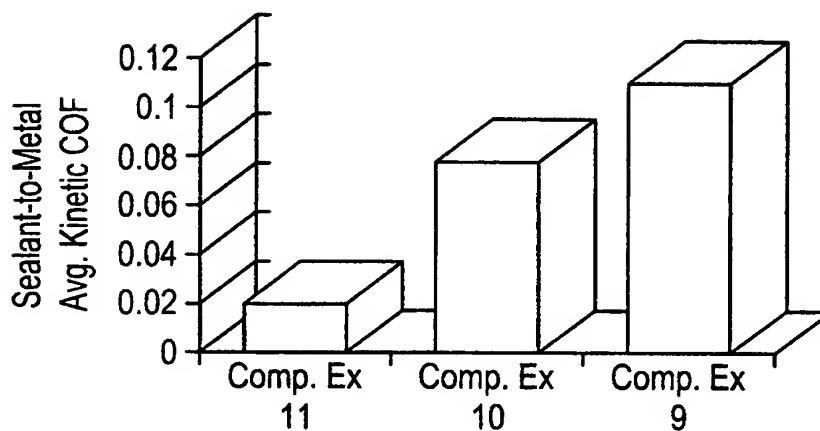


FIG. 17

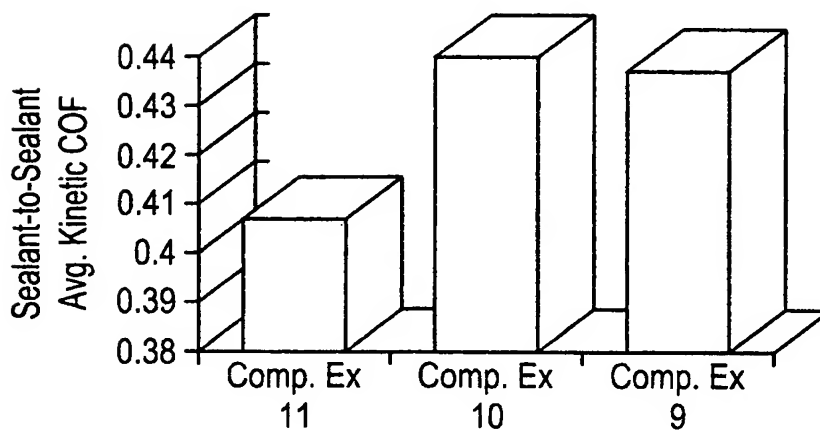


FIG. 18

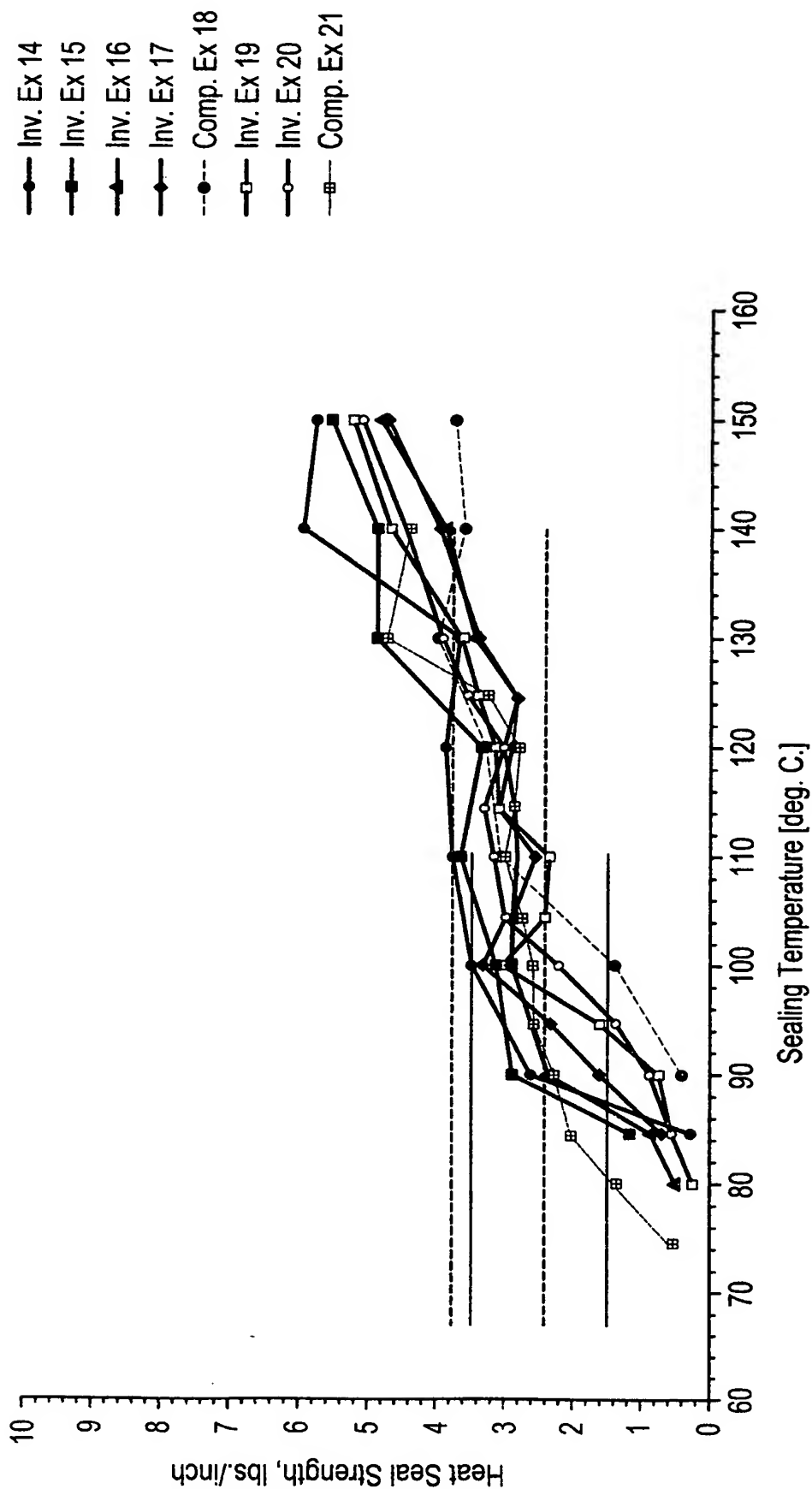


FIG. 19

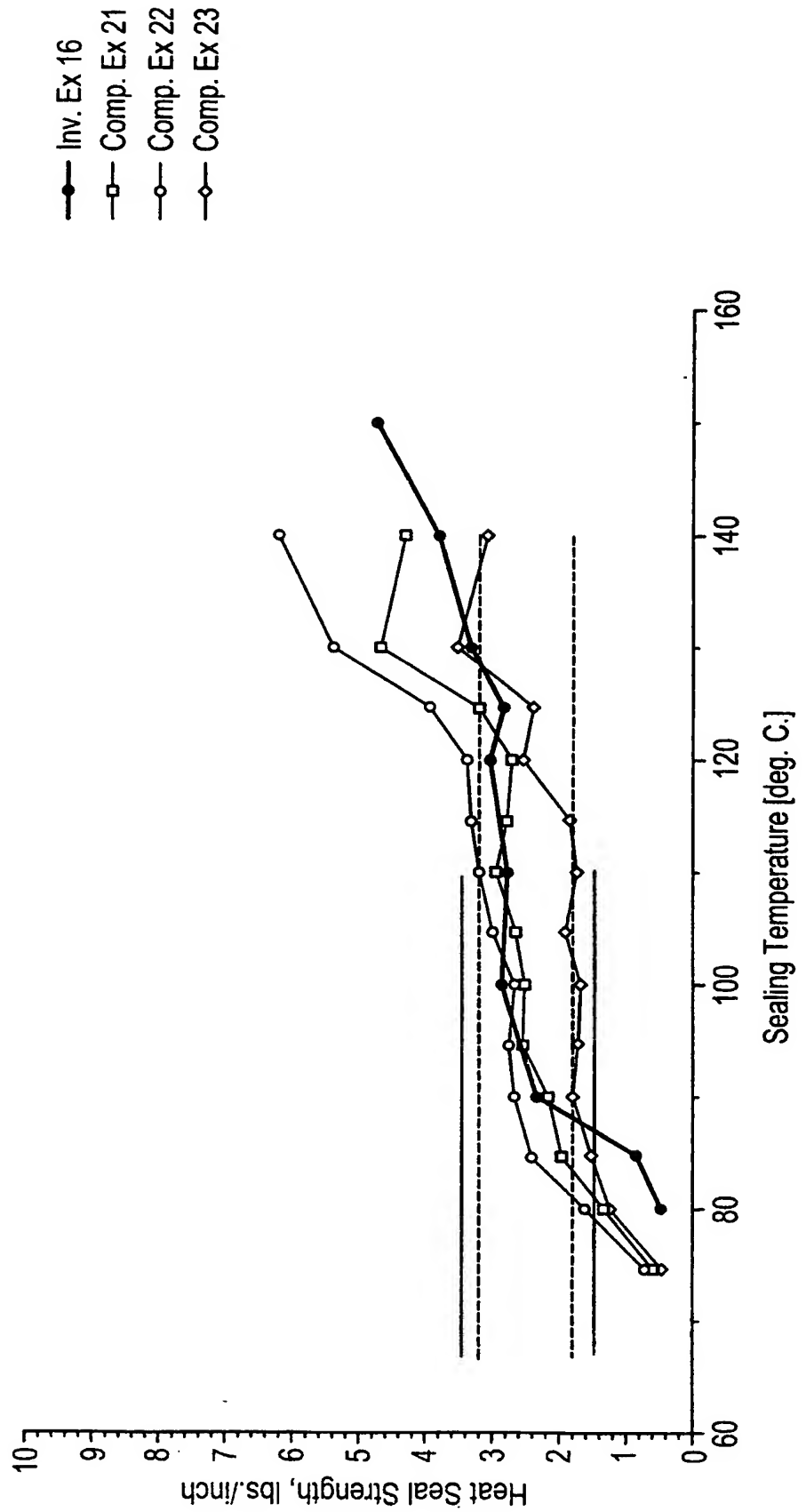


FIG. 20

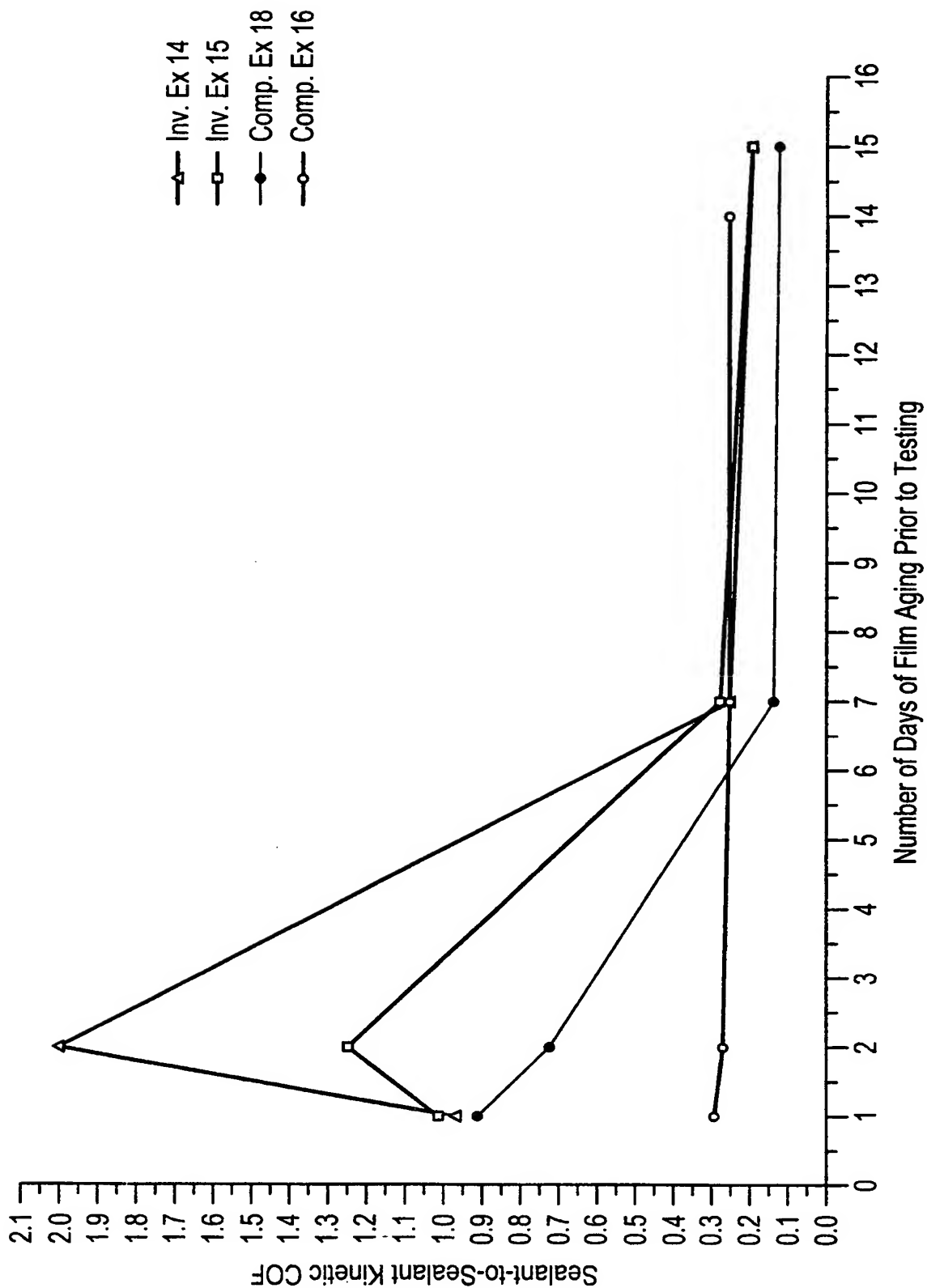
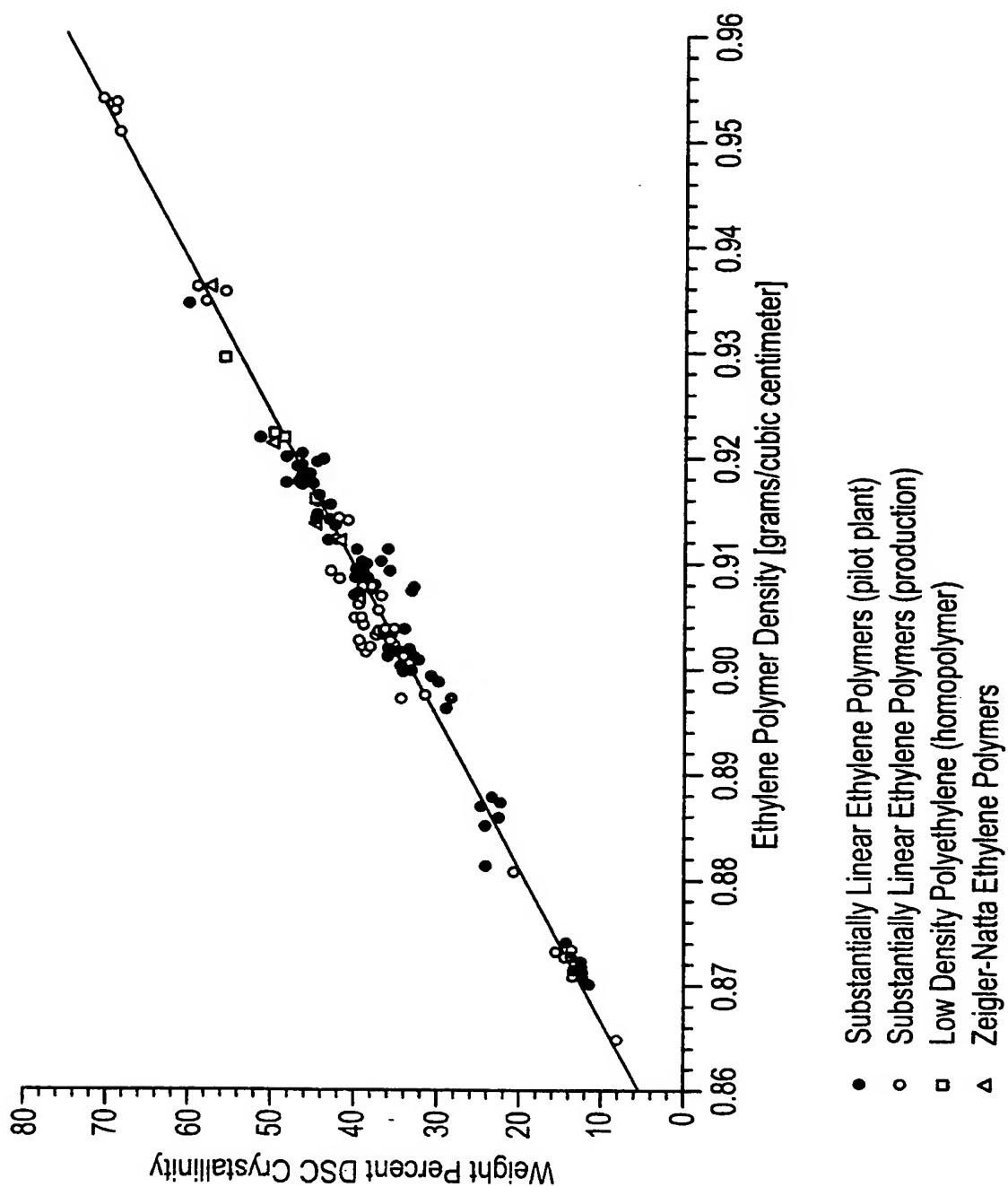


FIG. 21



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/08320

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J5/18 C08L23/16 //(C08L23/16,23:20)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C08L C09J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 48554 A (MERGENHAGEN LAURA K ;CHUM PAK WING S (US); DOW CHEMICAL CO (US); P) 24 December 1997 (1997-12-24)  page 3, paragraph 3 - page 5, paragraph 4 table 1 claims 1-3,6 page 6, paragraph 7 - page 7, paragraph 2 ---	1-11,16, 17,20, 21,23, 24, 35-37, 39-44
A	WO 96 12762 A (DEGROOT JACQUELYN A ;MERGENHAGEN LAURA K (US); STEWART KENNETH B () 2 May 1996 (1996-05-02) page 27, line 20 - page 27, line 23 page 29, line 3 - page 29, line 8 page 32, line 4 - page 32, line 5 --- -/-	1-45

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 August 1999

Date of mailing of the international search report

11/08/1999

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Authorized officer

Parry, J

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/08320

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 795 767 A (TURCZYK MICHAEL J ET AL)  3 January 1989 (1989-01-03)  page 3, column 3, line 34 - page 3,  column 3, line 37  -----</p>	25-27



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/08320

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